

CHEMISTRY

FOR CLASS XII

REPRODUCED



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CHEMISTRY

PART II
FOR CLASS XII

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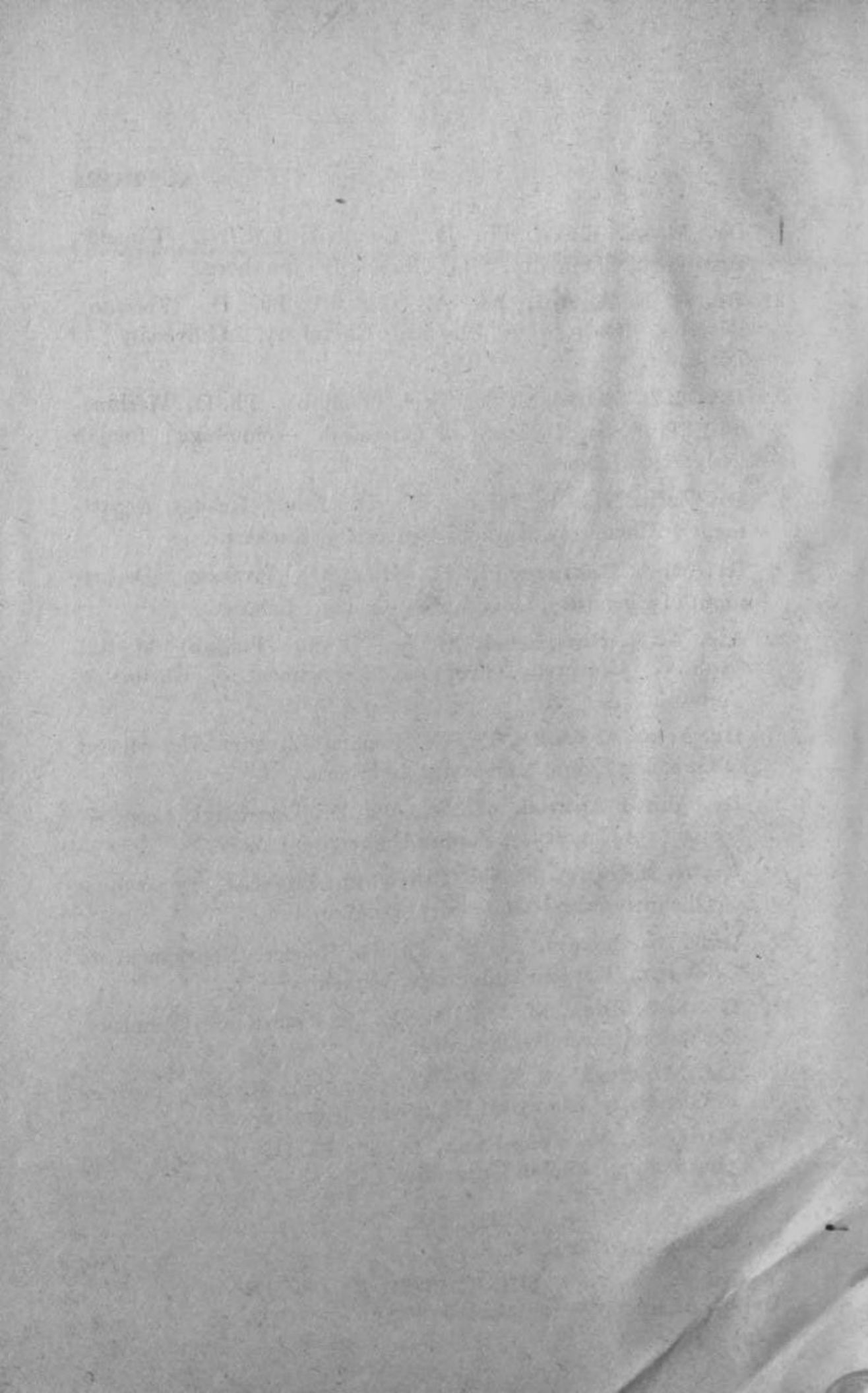
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PREFACE

In "Chemistry" Part I, modern concepts of chemical bonding, atoms, molecules, gases, liquids and changes of state and some of the fundamental principles such as chemical equilibrium and chemical kinetics, which govern chemical changes, were introduced. "Chemistry" Part II is a continuation of the first book in the sense that the basic principles introduced earlier have been extensively applied in discussing the chemistry of inorganic as well as organic compounds. With the great and rapid advances made in the field of chemistry during the past few decades an immense mass of facts of chemistry has been accumulated. It is neither the intention nor possible in a book of this size to present a great mass of uncorrelated facts and thus stress memory. The emphasis is on how the unifying principles of chemistry help in understanding and interpreting what is known and how reasonable predictions can be made about what is yet unknown. Chemistry is an experimental science and theoretical concepts are valid only if they stand the test of experiment. This book presents chemistry as a logical combination of fact and theory.

In the text books of chemistry used in our country the general pattern has been to discuss the occurrence, preparation and properties of substances, a wholly descriptive approach with no heed paid to unifying concepts. We have made a significant departure from the old pattern.

On the inorganic side comparative rather than isolated studies of the members of each group of the Periodic Table have been given. Tables of physical properties such as electronic configurations, atomic radii, ionization potentials, electronegativities and melting and boiling points are given and then gradation of chemical properties in going down a group correlated with these. Thus, for example, while discussing the group V of the Periodic Table it has been pointed out why nitrogen differs widely from other members of the group, why there is a gradual change from non-metallic to metallic character, why the oxides of nitrogen and phosphorus are strongly acidic, whereas the oxides of arsenic and stibium are amphoteric and those of bismuth largely basic. Again, for example, a comparative study of the hydrides of the group V elements has

been given rather than discussing the chemistry of ammonia, phosphine etc., independently. We believe this approach will help the student not only to understand the material presented but will also develop his ability to reason and to think. We have made it a point not to ignore the applied side of chemistry. Wherever possible reference has been made to processes of industrial importance *e.g.*, the manufacture of sulphuric acid, ammonia, and steel.

The Chapter on hydrogen includes a thought provoking discussion of the position of this element in the Periodic Table, and the chapter on water discusses, besides other aspects, the role of water as a solvent. An elementary discussion of the important concept of hydrogen bonding is also given in the same chapter. In chapter 10, a brief survey of the most recent chemistry of the Noble gases is presented. The purpose is to point out that chemistry is a growing science which cannot answer all of the questions raised by observation.

Chapter 11 is an introduction to organic chemistry. It discusses, in a systematic manner, the importance of organic chemistry, the reasons for treating the chemistry of organic compounds as a separate branch, and the analytical methods employed to develop the empirical, molecular and structural formulas of an organic compound. This chapter also introduces the concept of functional groups in order to familiarize the student with the various types of organic compounds at the very outset.

Chapter 12 discusses the modern concepts of the nature of chemical bond. Although some of the discussion in this chapter is a repetition of what has already been given in "Chemistry" Part I, these concepts have now been discussed with special reference to organic compounds. Also the chapter is extensively illustrated with diagrams. The terms "nucleophile", "*electrophile*" and "*ionic covalent bond*" have also been introduced and discussed. Chapters 11 and 12 will, therefore, lay down the foundation necessary for understanding the material presented in the subsequent chapters.

Chapters 13 through 18 discuss the chemistry of the various families of aliphatic compounds. The basic principles of earlier chapters are frequently used to indicate how and why chemical reactions occur. This should stimulate the interest of the student for further study and enquiry.

Since many of the readers of this text will choose medicine or engineering as their career and thus may not have the opportunity to take higher courses in chemistry, it was deemed necessary to give in this book a brief and elementary survey of the natural products which are so much a part of our daily life. This has been done in chapter 19.

The chapters in this book were initially written by a number of highly qualified and experienced teachers at the Universities of Karachi, Sind, Punjab and Peshawar. Their names appear in the beginning of this book. Their help and co-operation is greatly appreciated. In this connection we wish especially to thank Professor M. A. Kazi and Dr. Aejaaz A. Malik (Sind University), Dr. H. A. Kazmi (Peshawar University), Dr. Ghazi-ud-Din Ahmad (Karachi University), Dr. M. D. Shami of the Institute of Chemical Technology, Punjab University and Dr. M. A. Rehman of the Government College, Lahore.

Thanks are due to Vice-Chancellors for permitting the authors and editors to undertake this work, and encouraging them in the course of completing this assignment.

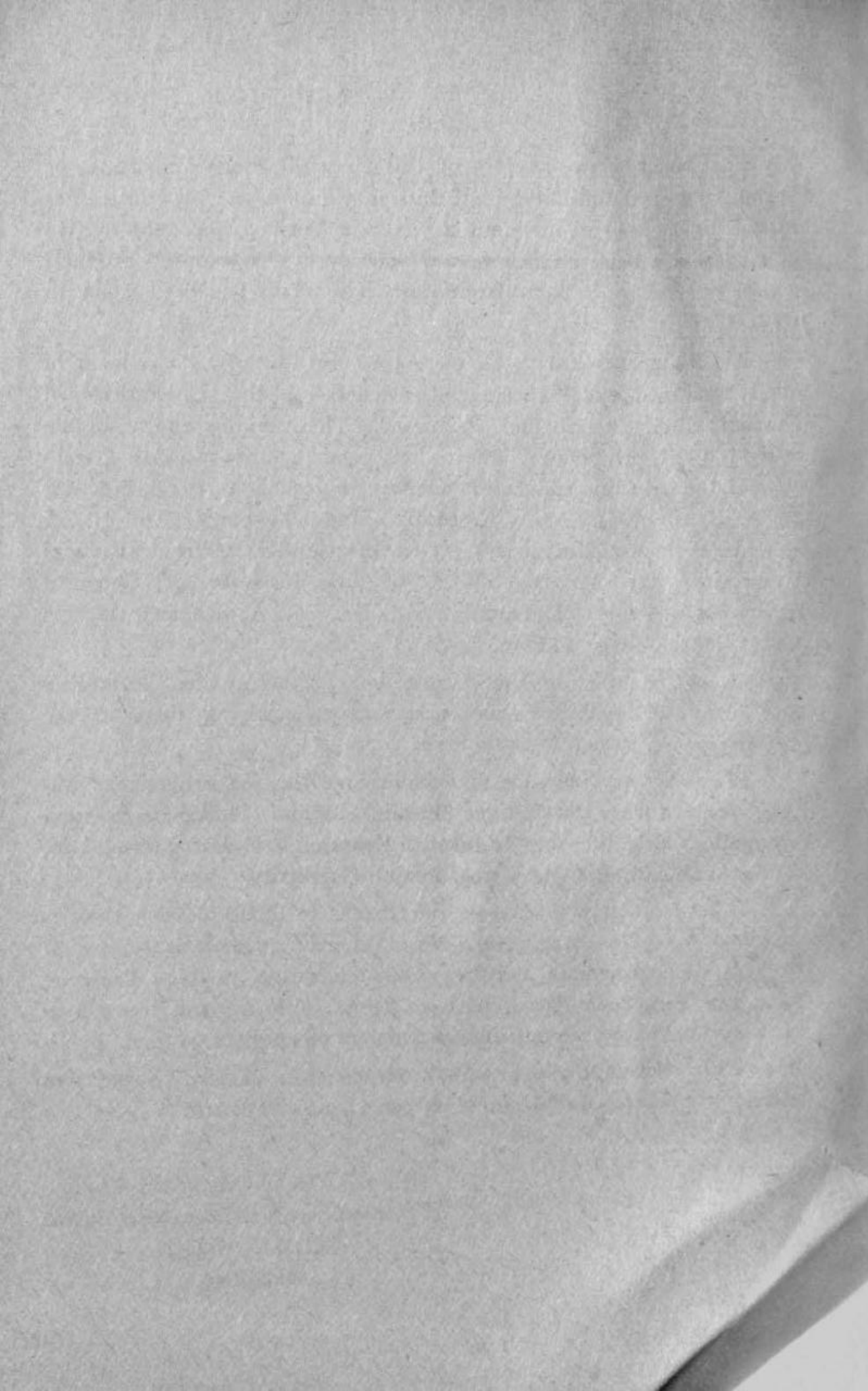
It is also our pleasure to acknowledge the support and inspiration received from Dr. Shafqat Hussain Siddiqui, Chairman, Pakistan Council of Scientific and Industrial Research and Dr. Badr-ud-Din, Director, Institute of Chemistry, Punjab University.

It is a pleasure to express our thanks to the Education Department of the Government of West Pakistan, the universities and boards of intermediate and secondary education in West Pakistan, and the Text Book Board, without whose initiative and active help it would not have been possible to complete this project on time.

This book will remain under our constant review. Suggestions for improvement would be most welcome from any quarter.

DR. KHAIRAT M. IBNE-RASA
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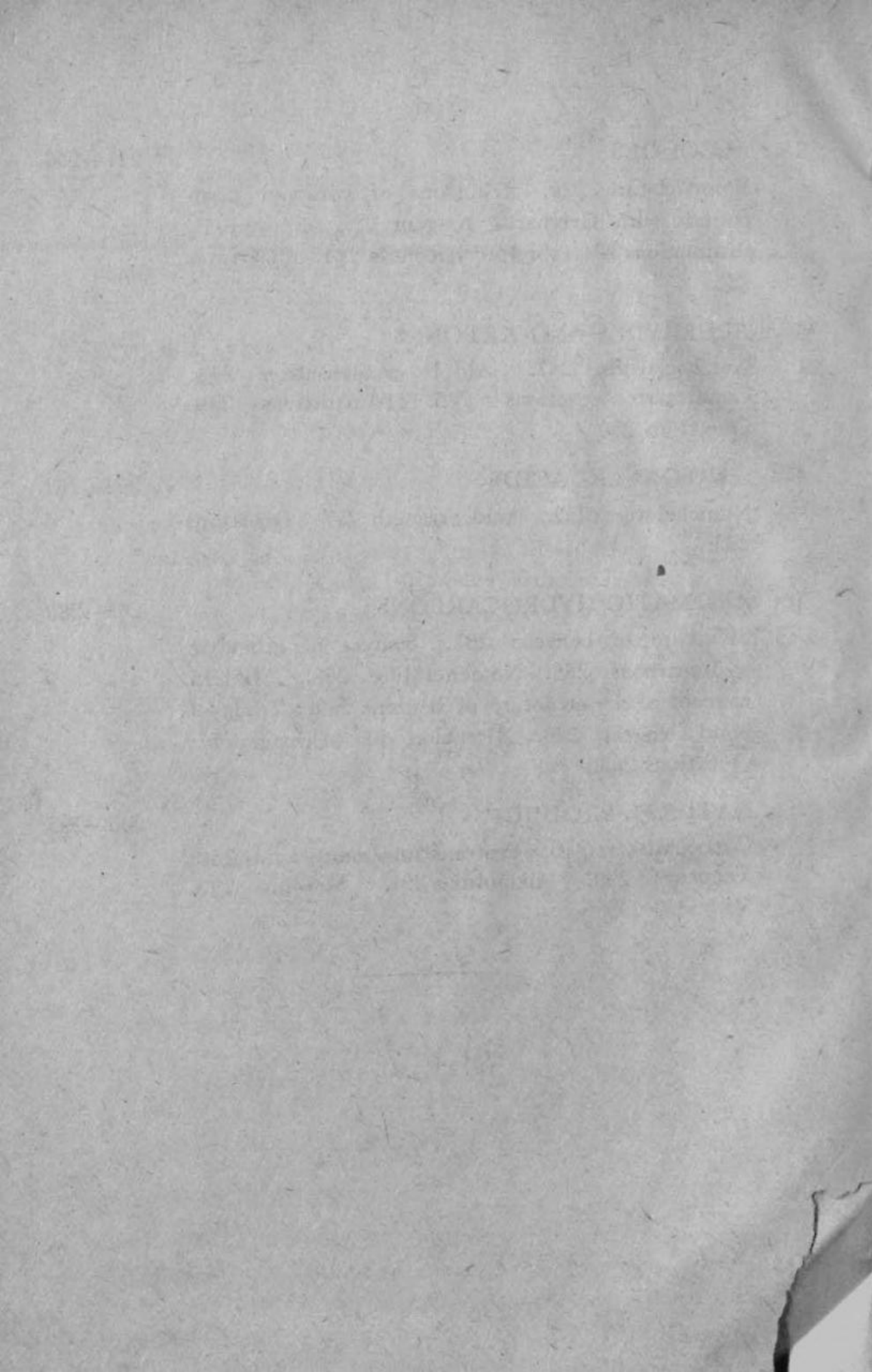


CONTENTS

Authors	.. (iii)
Preface	.. (v)
1. HYDROGEN	.. 1—8
Preparation 2. Physical constants of Hydrogen	
4. Binary compounds of H_2 5. Uses 6. Nascent hydrogen 7. Questions 8.	
2. WATER AND ITS SOLUTIONS	.. 9—22
Structure of H_2O 12. Water as a solvent 16.	
Hydration and hydrolysis 18. Reactions 20.	
Questions 21.	
3. LITHIUM AND BERYLLIUM FAMILIES	.. 23—32
The alkali metals 24. The alkaline earth metals	
25. Properties 25. Oxides and hydroxides 28.	
Carbonates and Bicarbonates 30. Questions 32.	
4. BORON AND ALUMINIUM	.. 33—42
Boron 35. Boric acid 36. Aluminium 37. Alums	
40. Questions 41.	
5. CARBON AND SILICON	.. 43—53
Electronic configurations of group IV elements 43.	
Carbon, diamond 44. Graphite 45. Reaction 48.	
Carbon dioxide 49. Silicon 50. Tin and lead 52.	
Questions 53.	
6. THE NITROGEN FAMILY	.. 54—75
Physical properties of group V elements 56.	
Hydrides 58. Oxides of V group 62. Oxyacids 67.	
Fixation of nitrogen 72. Questions 74.	
7. THE OXYGEN FAMILY	.. 76—95
Physical properties 77. Allotropy 79. Molecular	
structure 79. Hydrides 80. Oxides 83. Normal	
oxides, peroxides, superoxides and suboxides 85.	
Oxyacids 87. Thioacids 92. Questions 93.	

8. THE HALOGENS .. 96—106
 Occurrence and preparation 97. Properties 98.
 Oxyacids of the halogens 104. Questions 105.
9. THE TRANSITION ELEMENTS .. 107—129
 Physical properties 108. Complex formation 112.
 Iron 119. Nickel 124. Copper 125. Questions 128.
10. NOBLE GASES .. 130—134
 The inert gases become reactive 131. Compounds
 of noble gases 132. Questions 134.
11. INTRODUCTION TO ORGANIC CHEMISTRY .. 135—157
 Sources 139. Structural formulas 140. Detection
 of elements 141. Empirical formula 144. Mole-
 cular weight 145. Classification of organic com-
 pounds 148. Functional groups 151. Questions
 155.
12. THE NATURE OF THE CHEMICAL BOND .. 158—183
 The types of chemical bond 158. Orbitals of the
 hydrogen atom 164. The Pauli exclusion Principle
 166. Hund's rule 167. Orbital hybridizations 173.
 Ionic character of covalent bonds 178. Electro-
 philes and nucleophiles 180. Acids and bases 181.
 Questions 182.
13. HYDROCARBONS .. 184—207
 Isomerism 186. Unsaturated hydrocarbons 186.
 Nomenclature 188. Saturated hydrocarbons 191.
 Synthesis of alkanes 192. Synthesis of alkenes
 197. Addition reactions of alkenes 199. Mar-
 kownikoff's rule 200. Alkynes 202. Acidic nature
 of acetylene 204. Questions 205.
14. MONOHALO-ALKANES .. 208—223
 Nucleophilic substitution reactions (SN) 209.
 Elimination reactions 213. Aliphatic amines 215.
 Reactions with nitrous acid 218. Ethers 219.
 Questions 221.

15. ALCOHOLS .. 224—236
Nomenclature 224. Reactions of carbonyl compounds with Grignards reagent 226. E_1 and E_2 eliminations 234. Simple Alcohols 234. Questions 235.
16. ALDEHYDES AND KETONES .. 237—251
Nomenclature 237. Aldol condensation 244. Cannizzaro reactions 245. Preparations 249. Questions 250.
17. CARBOXYLIC ACIDS .. 252—262
Nomenclature 252. Acid strength 257. Questions 262.
18. AROMATIC HYDROCARBONS .. 263—285
Structure of benzene 263. Sources of aromatic hydrocarbons 266. Nomenclature 268. Modern concept of the structure of benzene 269. Table of bond lengths 273. Nitration of benzene 277. Questions 283.
19. NATURAL PRODUCTS .. 286—295
Carbohydrates 286. Proteins and amino acids 288. Terpenes 290. Alkaloids 291. Steroids 292. Vitamins 293.
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CHAPTER 1

HYDROGEN

Hydrogen is the lightest of all the elements known. Its atom possesses a proton in the nucleus and a single electron in the $1s$ orbital. It is represented by the symbol H and is also known as protium. Besides this ordinary form of hydrogen, which occurs most abundantly in nature there are two other isotopes known as deuterium, ${}_1H^2$ or D and tritium, ${}_1H^3$ or T . Deuterium with mass number 2 contains one neutron and one proton in the nucleus while tritium atom having mass number 3 contains two neutrons along with one proton in the nucleus. However, they all have the same electronic configuration $1s^1$.



Three Isotopes of Hydrogen

Fig. 1.1

Hydrogen was discovered by Cavendish in 1766. He found that the reaction between a metal and a dilute acid produces a gas which was highly inflammable. *produced*

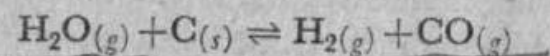
Occurrence : Hydrogen is generally found in the combined state in the form of its compounds with oxygen, carbon, nitrogen and sulphur, the most abundant of which is water. Other important compounds of hydrogen include hydrocarbons which occur in petroleum and natural gas. Most of the known organic compounds contain hydrogen as one of the constituent elements.

Free hydrogen occurs in small amounts in earth and its atmosphere. There is spectroscopic evidence that large amounts of atomic hydrogen are present in the atmosphere of the sun and most of the stars.

PREPARATION :

Industrial Preparation : Hydrogen is prepared on industrial scale from its compounds such as water and hydrocarbons. These compounds occur most abundantly in nature.

(a) **From Water :** (i) When steam is passed over coke at about 1000°C , a mixture of carbon monoxide and hydrogen is produced. This mixture is called water gas.

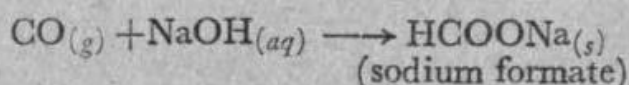


(ii) These products are also obtained when steam is mixed with natural gas (hydrocarbons) in the presence of a catalyst.

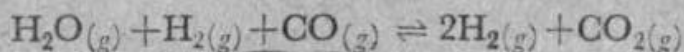


(a constituent of natural gas)

Carbon monoxide is separated by liquefaction (at -192°C) with liquid air. The last traces of CO are removed by passing it over soda lime.

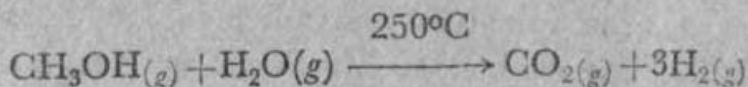


More commonly hydrogen is separated from water gas by reacting it with steam at about 500°C in the presence of a catalyst (iron oxide or cobalt oxide) to produce a mixture of carbon dioxide and hydrogen.

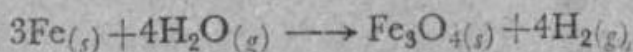


Carbon dioxide is separated easily by dissolving it in water under pressure leaving behind pure hydrogen.

(iii) The catalytic decomposition of methanol with steam also produces hydrogen and carbon dioxide.



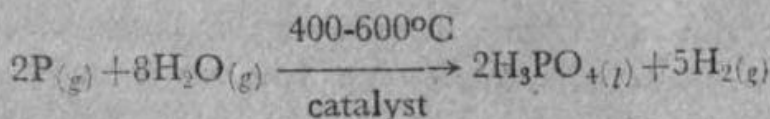
(iv) Hydrogen gas in relatively pure state is also prepared by passing steam over finely divided hot iron.



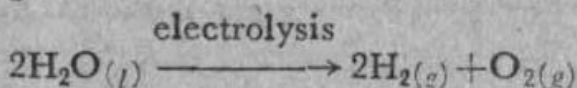
The magnetic oxide (Fe_3O_4) produced in this reaction is treated with water gas to regenerate iron for further use.



In the Liljenroth-process phosphorus is used instead of finely divided iron to decompose steam.

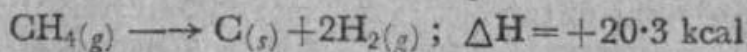


(v) The electrolysis of water produces hydrogen gas in the purest form. This electrolytic decomposition of water is carried out usually in the presence of a strong base like NaOH which serves as an electric current carrier. Oxygen gas is obtained as a by-product at the anode whereas hydrogen gas is collected at the cathode.



This process is very expensive due to large consumption of electric power.

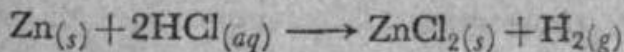
(b) **From other compounds :** Hydrogen is commercially prepared by the thermal decomposition of methane. A mixture of natural gas and air is burned in a firebrick furnace to bring the temperature up to 1200—1400°C. The air supply is then cut off and the passage of natural gas is continued, when the decomposition occurs :



It can be obtained from coke-oven gas by fractional liquefaction. Moreover hydrogen is also obtained Industrially as a by-product in the electrolysis of NaCl and in the preparation of acetylene.

Laboratory preparation : Hydrogen is produced in the laboratory by the action of dilute acids, bases and water on metals.

(i) Dilute acids react with metals like iron, zinc and aluminium to produce hydrogen.

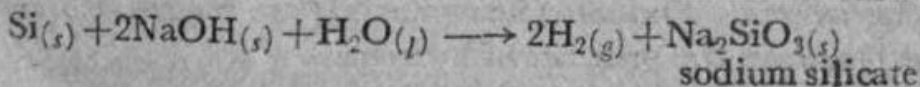
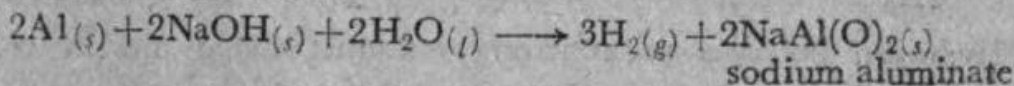


These metals are more electropositive than hydrogen.

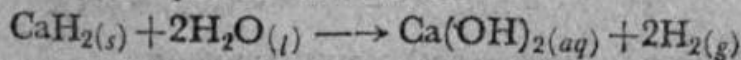
(ii) Alkali metals and alkaline earths (strontium, calcium, barium), which are more electropositive than zinc and iron, etc., react vigorously with dilute acids as well as with water to liberate hydrogen gas and their respective hydroxides are formed. The reaction of water with zinc is exceptionally very slow.



(iii) Some of the metals like tin, aluminium, zinc and non-metals like silicon displace hydrogen from the aqueous solutions of strongly basic hydroxides such as NaOH.



(iv) A very convenient method for the preparation of hydrogen gas is the reaction of calcium hydride with water.



Properties : Hydrogen is a gas at normal temperature and pressure with molecular formula, H_2 and atomic weight 1.008. It is colourless, odourless, tasteless and almost insoluble in water. It burns in air with a bluish and very hot flame. It has a remarkable property that it can be absorbed on the surface of various metals such as platinum and palladium like sponge and can be recovered quantitatively on heating the metal at a suitable temperature. The phenomena being known as adsorption. The following Table (1.1) gives some of its physical constants.

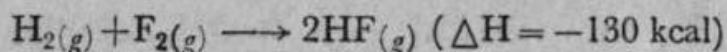
Table 1.1

PHYSICAL CONSTANTS OF HYDROGEN

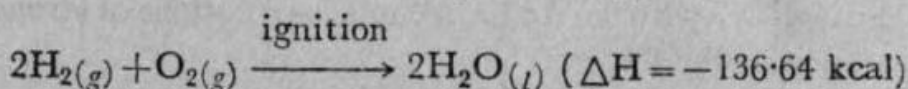
melting point	..	14.1°K
boiling point	..	20.4°K
critical temperature	..	33.2°K
density at STP	..	0.0899 g/l
density of liquid (20°K)	..	0.07 g/l
atomic volume of solid	..	13.1 ml/mole of atoms
bond energy	..	103 kcal/mole
bond length	..	0.749 Å°
ionization potential	..	13.54 e.v.
electron affinity	..	0.72 e.v.

Chemical properties : Decomposition of molecular hydrogen into hydrogen atoms does not occur at ordinary temperatures, because of a very stable hydrogen-hydrogen covalent bond. However, the reaction velocity is quite appreciable at higher temperatures, where the hydrogen molecule decomposes into its atoms. At 7000°K the decomposition of $H_{2(g)} \longrightarrow 2H_{(g)}$ is complete.

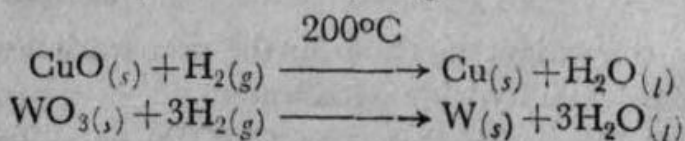
Hydrogen reacts directly with halogens to give hydrogen halides,



Hydrogen also combines directly with oxygen to form water.



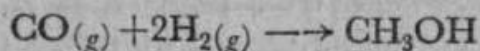
Hydrogen behaves as a strong reducing agent due to its great affinity for oxygen. Oxides of heavy metals are reduced to metals when they are heated in the presence of hydrogen.



The last reaction is used to obtain pure tungsten.

Compounds like palladium (II)-chloride are reduced by hydrogen gas at ordinary temperature.

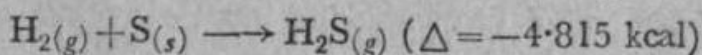
Hydrogen combines directly with some compounds to form addition products e.g.,



This type of reaction is known as hydrogenation. Such reactions occur mostly at high temperature and pressure in the presence of catalyst. The hydrogenation of vegetable oils to solid fats (*Banaspati ghee*) is its typical industrial application. This process is carried out in the presence of finely divided nickel as a catalyst.

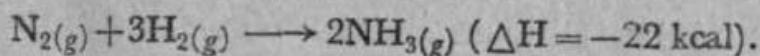
Reduction and hydrogenation take place at ordinary temperatures when substances such as platinum black or palladium are present as catalysts.

Hydrogen reacts with sulphur to produce hydrogen sulphide.



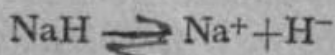
This reaction takes place at high temperature. Hydrogen sulphide has the same electronic configuration as water.

Nitrogen reacts with hydrogen to form ammonia

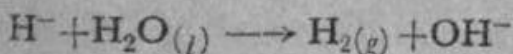


This reaction is very slow and reversible at ordinary temperatures. To accelerate the formation of ammonia higher temperature and pressure alongwith a catalyst (iron oxides) are required (Haber Process).

Binary Compounds of Hydrogen : Hydrogen reacts with some elements to form binary compounds which are called *hydrides*. Some of these hydrides have ionic characters like salts. They are known as salt-like hydrides. Their typical examples are the hydrides with alkali metals and calcium, strontium and barium. They are formed by the direct combination of the metal and hydrogen at high temperatures (between 150—700°C) depending on the metal used. Saltlike hydrides are solids and decompose electrolytically in molten condition to form the metal cations and hydride anions.



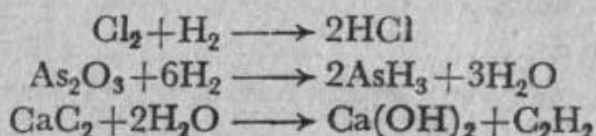
The H^- being unstable reacts immediately with water to form hydrogen and hydroxyl ion.



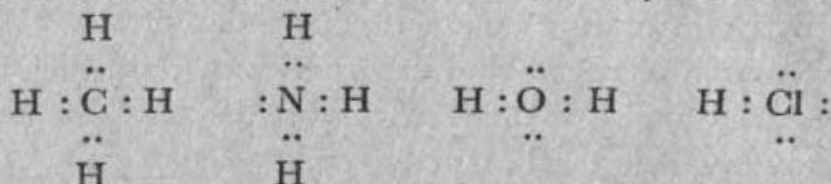
Hydrogen reacts with the non-metallic elements of IV ; V ; VI and VII

groups to form covalent hydrides. They may be prepared by direct combination or by suitable reduction reactions.

For example :

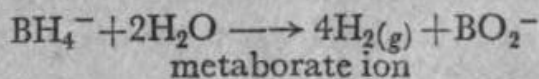


The electronic structures of some of the covalent hydrides are :



These compounds are usually gaseous at ordinary temperatures. The hydrides of the elements of VI and VII groups lose hydrogen more easily as the size of the element increases. This order of decreasing stability is also observed when they are thermally decomposed. This weakness in H—X bond is due to the increasing atomic radii of the elements.

The elements of group III combine also covalently with four atoms of hydrogen instead of three. These compounds have a negative charge in excess and because of that they form salts like NaBH_4 (sodium borohydride), and LiAlH_4 (lithium aluminium hydride). These hydrides are known as complex hydrides. They are solids having tetrahedral structure and liberate hydrogen when reacted with water.



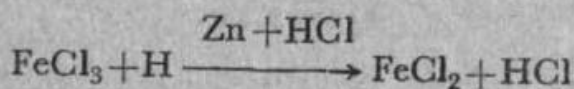
These are powerful reducing agents ; LiAlH_4 is used as an important reducing agent in organic chemistry.

Another class of hydrides is the metallic hydrides. These substances are very often non-stoichiometric with formulas such as $\text{LaH}_{2.76}$, $\text{CeH}_{2.69}$, $\text{TaH}_{0.76}$ and $\text{VH}_{0.56}$. They are generally formed by the transition metals, when they absorb hydrogen or when such metals are used as cathodes where hydrogen is evolved. The properties of such hydrides are not very different from those of the metals themselves. Much of the hydrogen in these hydrides is lost on heating, and it appears that the gas may be contained in the spaces between the atoms in the crystals of the metals.

- Uses :**
- (1) Hydrogen being the lightest of all gases (14 times lighter than air) is used in filling weather balloons.
 - (2) Hydrogen is also used in *Industry* to prepare edible fats from vegetable oils by the process of hydrogenation.

- (3) Liquid hydrogen is used to produce low temperatures.
- (4) Water gas (a mixture of H_2 and CO) is used in industry for heating purposes.
- (5) It is also used in industry for the synthesis of ammonia, hydrochloric acid, methanol and hydrocyanic acid.
- (6) It is also used in the production of tungsten filaments for electric lamps.
- (7) Oxy-hydrogen flame is very hot and is used to cut and weld the metals.

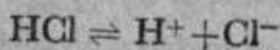
Nascent Hydrogen : Hydrogen being in atomic state, at the time of its formation is more reactive than ordinary hydrogen. For example, the reduction of ferric chloride to ferrous chloride takes place readily when zinc is added to acidified solution of ferric chloride.



Similarly the alkyl cyanides are reduced readily to primary amines with sodium metal and absolute alcohol. On the other hand the reduction of these compounds is very slow when hydrogen gas is used as reducing agent. The atomic hydrogen at the time of its generation from a chemical reaction is usually called nascent hydrogen.

Position of Hydrogen in the Periodic Table : Hydrogen is placed in the periodic table above alkali metals (group I) and sometimes above halogens (group VII). This classification is based upon its electronic configuration as well as its properties common with these elements. However this classification is not justified if we go into details.

Hydrogen resembles alkali metals only in possessing one electron in the valence shell, but it differs from them in its physical and chemical properties. It is a gas at ordinary temperature and behaves mostly as a non-metal in forming covalent bonds (HF ; NH_3 ; H_2O). Moreover hydrogen needs only one electron instead of seven to acquire the electronic structure of the next noble element (helium). It would tend to attract or share one electron to have its maximum capacity ($1s^2$) rather than to lose its single electron which is strongly attracted to the positively charged nucleus. It forms compounds with non-metals (HF : HCl) and their aqueous solutions ionize to form hydrogen cations.



But these H^+ ions unlike Na^+ ions do not exist except in the solvated form as H_3O^+ or $H_9O_4^+$.

By attracting one electron hydrogen combines with metals to form salt-like hydrides thus resembling halogens. Alkali metal hydrides particularly have cubic structures like that of NaCl and they are ionic in nature. But unlike Cl^- , H^- is incapable of existence in water, since H_2 is formed immediately and there is also no stabilization due to solvation.

It is very interesting to note that the valence shell of hydrogen is half filled, like that of carbon; the half filled valence shells of hydrogen and carbon acquire their maximum capacities by sharing electrons through covalent bonding. Moreover thermodynamic properties (ionization energy, electron affinity) of hydrogen are also similar to that of carbon and other group IV elements. In view of this hydrogen should probably be placed above group IV-A.

Questions

1. How many isotopes of hydrogen are known? How do these differ in structure?
2. Hydrogen combines with other elements in two ways. Illustrate them giving appropriate examples.
3. Are the chemical reactions of molecular hydrogen ordinarily slow or rapid? Why? What is nascent hydrogen?
4. Draw electronic structures of the common binary compounds formed by hydrogen with (a) nitrogen, (b) silicon and (c) sulphur.
5. Write notes on :
 - (a) hydrogenation and reduction,
 - (b) nascent hydrogen,
 - (c) salt-like hydrides and
 - (d) position of hydrogen in the Periodic Table.
6. Write balanced equations for the reactions between :
 - (a) hydrogen and iodine.
 - (b) CuO and hydrogen.
 - (c) CO and hydrogen.
7. Which of the following compounds would you choose as a source for preparing hydrogen?
Lithium hydride, sodium hydride and calcium hydride.
8. The simplest ions of hydrogen are H^+ and H^- . Do they exist as such in an ordinary chemical reaction? What would be their behaviour with water?

CHAPTER 2

WATER AND ITS SOLUTIONS

Introduction : Water is most extensively used for washing, drinking and cooking in every day life. It is also used in great quantities in industries for various purposes. Water occurs abundantly around us in liquid form or as solid (ice and snow). More than half of the earth's surface is covered with water. Water is found under the earth, in combination with salt and minerals and entrapped between empty spaces in rocks and certain crystalline structures.

Water is a must for life, and wherever living organisms are present, water is invariably found with them. Human body contains nearly 70% water. In vegetable kingdom, water is present in various plants from 50—80%.

Water is an excellent solvent, and due to this property it is employed to dissolve a great variety of solids, liquids and gases. In the laboratory, it is used as a solvent for many inorganic and some organic chemicals and many chemical reactions are carried out in it.

Water, due to its great dissolving power, occurs in nature in an impure state. Water in wells, rivers and seas contains dissolved chlorides, sulphates, carbonates and bicarbonates of sodium, potassium, calcium and magnesium. Water used for washing purposes, which contains the above-mentioned impurities, is known as hard water. Sometimes these impurities can be easily removed by heating or boiling and the hardness is said to be temporary. In other cases, the impurities are difficult to remove and distillation, precipitation or ion exchange techniques may be used to purify water. This water is termed as permanently hard. Temporary hardness is essentially due to dissolved bicarbonates while permanent hardness is due to dissolved chlorides and sulphates.

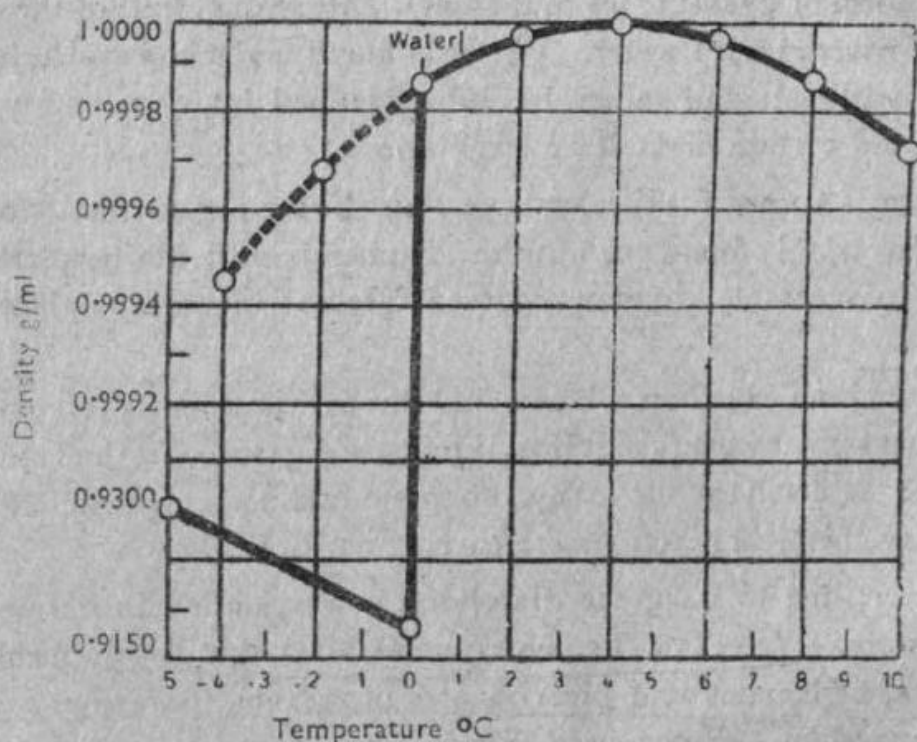
Besides, water contains dissolved compounds of sodium and metals like gold and silver.

Solid, Liquid and Vapour : We are accustomed to see water in three states, namely solid, liquid and vapour. Solid water is called ice or snow; liquid water is called just water and vapour water is known as steam.

Let us look more carefully into the three states of water and see how one state can be converted to the other? What changes in properties are observed when water changes its state?

Ice floats over water indicating that ice is lighter than water. In other words, the density of ice is less than the density of water. As the temperature of ice rises the ice melts and its density increases. The density of water is maximum at 4°C , Fig. 2.1.

The figure also indicates that the density of liquid water at 0°C is somewhere between 0.9990 and 1.000, while the density of ice at 0°C is



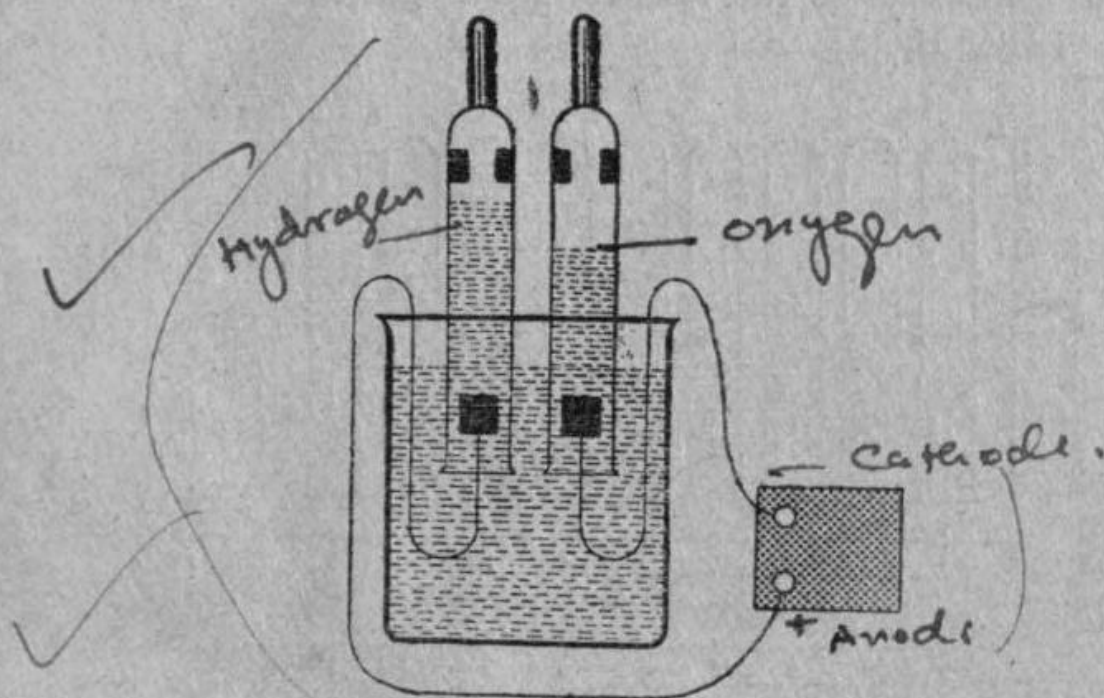
The effect of temperature on the density of liquid water.

Fig. 2.1

of the order 0.918. Therefore, there is a considerable increase in volume when liquid changes to solid at 0° . In terms of the molecular model, we can say that water molecules are less tightly packed (are at greater distances) in ice than in liquid water. This point will be considered again in the structure of water. The fact that water contracts on heating within the temperature indicated is quite contrary to the behaviour of many of the other liquids. This property helps nature to preserve fish and other living animals in water in countries where freezing of water takes place during winter. When cooling of water starts, as winter approaches, the density of water increases until it reaches its maximum (density 0.0000 g/ml) at 4°C . Thus water is heavier at 4°C and sinks to the bottom. Further cooling, cools down the surface layer below 4°C and

since the density of water now is lower than the water at 4°C it stays at the top and is frozen to solid ice, while the liquid below remains at 4°C . Dissolved air helps animals to breath and thus they spend a nice winter under a thick blanket of ice.

Pure water does not conduct electricity. However, when current is passed through acidulated water, it breaks up into two gaseous components, hydrogen and oxygen. This can be done in an electric



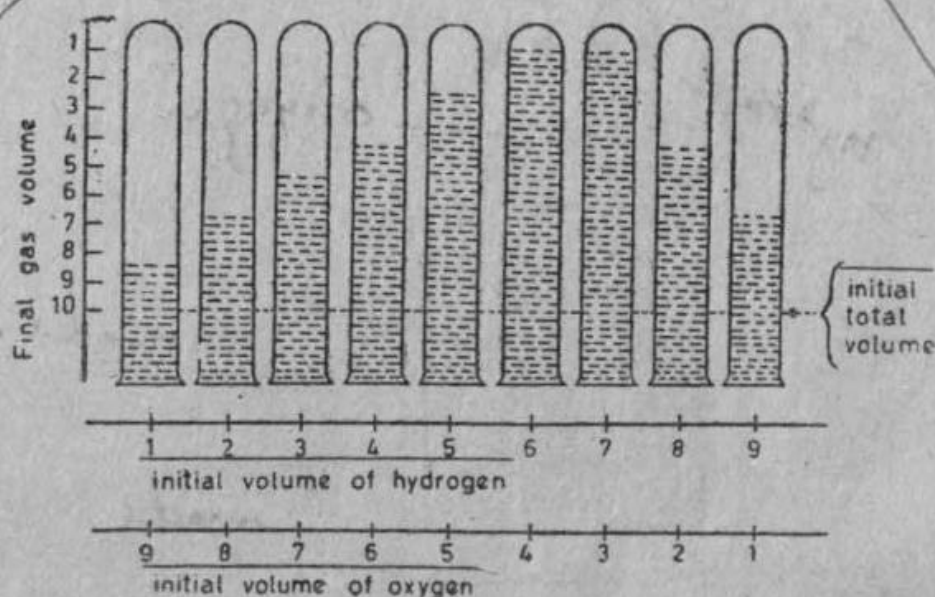
Apparatus for the electrolysis of water.

Fig. 2.2

cell shown in Fig. 2.2. If current is passed for a sufficiently long time it is observed that the volume of the two gases collected is in the ratio 1:2, where the volume of hydrogen is double that of oxygen. If we use Avogadro's hypothesis, we can deduce that a water molecule should contain double the number of hydrogen atoms than oxygen atoms. Hence the formula for a water molecule is H_2O .

A more accurate experiment is the one in which hydrogen and oxygen are made to combine to give water. This may be done by taking different compositions of hydrogen and oxygen and subjecting them to an electric discharge. Consider the compositions shown in Fig. 2.3 (a). All the tubes are fitted with a platinum filament attached to a battery. When an electric discharge is passed, combina-

tion between hydrogen and oxygen takes place with an explosion. After the reaction is over and the temperature is brought back to room temperature, it is noticed that water has risen in all the tubes. The rise in water indicates that the gases in these tubes were used up and water was formed. Water rises more in tubes where percentage of hydrogen and oxygen was favourable to produce H_2O . In fact if volume of gases used is plotted against percentage of the gases by volume a graph as in Fig. 2.3 (b), is obtained which shows a maximum of oxygen at 33.3%, and this corresponds to two volumes of hydrogen and one volume of oxygen yielding H_2O .

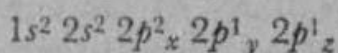


Gaseous product from the reactions of hydrogen and oxygen systems. Volume of each gas before reaction are shown on the scales below the test tubes.

Fig. 2.3 (a)

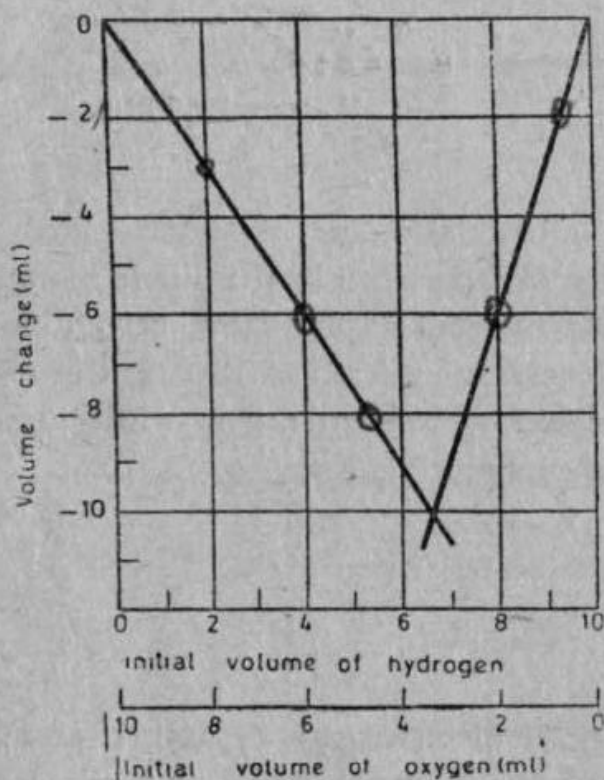
Structure of Water : Let us assume that oxygen forms the central atom while two hydrogen atoms bond with it one on each side giving HOH.

Electronic structure of oxygen is (At. No. 8)



and thus oxygen can use its two p orbitals (p_y and p_z) with one electron each to share an overlap with $1s$ orbital of hydrogen. The structure may be represented as in Figure below. This would give an angle of 90° between two hydrogen atoms. The measured angle is 104° . This

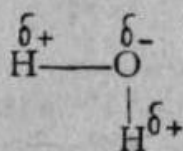
may be explained in terms of electronegativities of oxygen and hydrogen. Since oxygen is more electronegative than hydrogen, a partial negative



Initial volume of Oxygen, ml.
Volume change, measured at 20°C, for the reaction
of hydrogen and oxygen mixtures.

Fig. 2.3 (b)

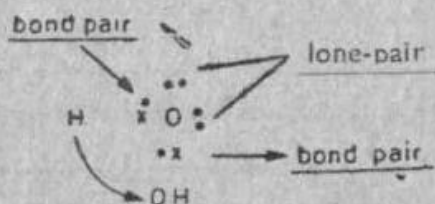
charge results on oxygen and a partial positive charge on hydrogen giving :



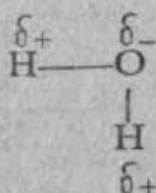
Two positive charges repel each other and open the angle to 104°. An alternative picture, which has explained the angle more precisely is to consider the water molecule as tetrahedral.

The O atom of the H₂O molecule may use four non-equivalent *sp*³ hybrid orbitals, two for the O—H bond pairs and two for the lone pairs. The direction, in space, of the four hybrid orbitals remains essentially tetrahedral. The H—O—H bond angle of 104.5° may be explained

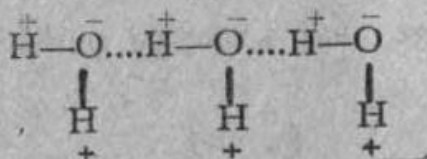
on the fact that the lone-pair—lone-pair repulsion is stronger than the lone-pair—bond-pair repulsion.



The idea of a bent structure of water as compared to linear H—O—H , is further strengthened by the dipole moment of water. We know that a linear molecule would have zero dipole since electron distortions are balanced in such a way that centres of the negative and positive charges coincide giving zero dipole, while a bent water molecule would show a dipole as given below.



Due to its greater electronegativity oxygen atom would accumulate more charge on it giving the molecule a dipole moment of 1.80 Debye. It is interesting to note the high melting point, boiling point, heat of fusion and heat of vaporization of water, as compared to H_2S , H_2Se and H_2Te . This is commonly explained in terms of hydrogen bonds formed among water molecules due to dipole interactions, as shown in Figure below.



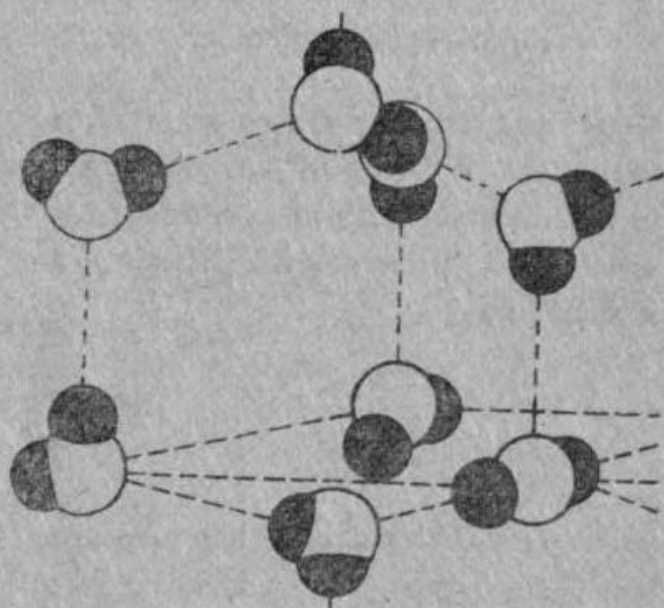
These bonds are much weaker than covalent bonds between oxygen and hydrogen. The energy required to break all the hydrogen bonds in 1 mole of liquid water is about 7 kcal/mole whereas the energy required to break one of the covalent bonds within a water molecule is about 110 kcal per mole. Energy has to be spent to separate water molecules (to break hydrogen bonds) and hence a high value of heat of fusion and heat of vaporization, is observed (Table 2.1). Similarly when ice melts to liquid or liquid is heated to steam, hydrogen bonds are broken, which needs the expenditure of thermal energy. This explains as to why the melting point and boiling point of water are unusually

higher than those of other hydrides of the same group (see Table 2.1).

Table 2.1

Substance	b.p. °C	m.p. °C	Heat of fusion kcal/mole	Heat of vaporization kcal/mole
Water	100	0.0	1.44	9.72
Hydrogen sulphide	-60.3	-85.5	0.57	4.46
Hydrogen selenide	-41.3	-65.7	0.60	4.62
Hydrogen telluride	-2.2	-51	1.0	5.55

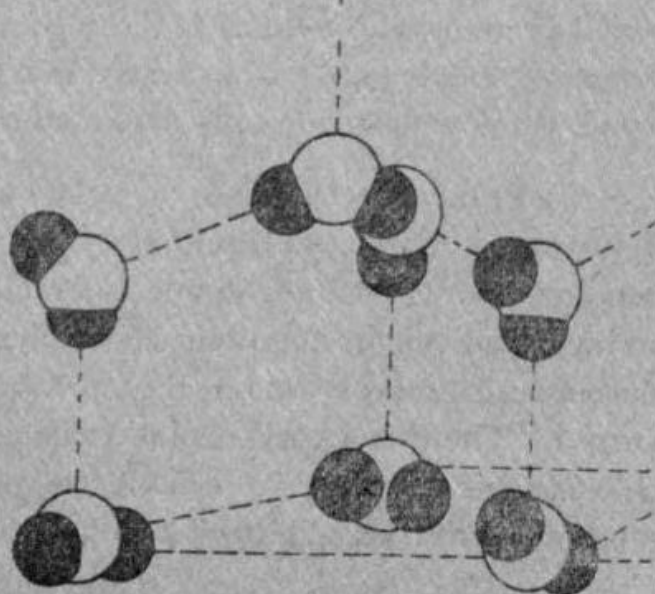
At 0°C water freezes to ice. Ice has a molecular crystal lattice in which each H_2O molecule has four nearest neighbours. The O atom



The crystal structure of ice.

Fig. 2.4

The overall structure of ice may be seen as in Fig. 2.4.



of each H_2O molecule is tetrahedrally surrounded by two different pairs of H atoms : With the two closest H atoms it forms covalent bonds and with the other two H atoms it forms hydrogen bonds. In turn each H atom is joined to two O atoms : with the one it forms a covalent bond and with the other it forms a hydrogen bond. This results in an 'Open' net work structure having considerable empty spaces between the molecules and hence lower density of ice as compared to liquid water. When ice melts, some of the hydrogen bonds are broken and so does the open network structure.

(i) **Water as a Solvent :** Water dissolves a majority of inorganic compounds. Quite a number of organic compounds are also soluble. This property of water that it dissolves a little bit of everything is explained by two factors :

- (i) high dielectric constant; and
- (ii) polarity of molecule.

Water has a dielectric constant of 80. Dielectric constant determines the extent of forces of attraction between oppositely charged particles in a dielectric medium as compared to those forces in a vacuum. Force of attraction between two charges q_1 and q_2 in a medium at a distance r is defined as

$$F = -\frac{q_1 q_2}{\epsilon r^2}$$

where ϵ is dielectric of that medium. It equals one for vacuum, and it is 80 for water. It means that forces of attraction between q_1 and q_2 would be reduced 80 times if these charges are immersed in water as compared to vacuum. Thus water, due to its high dielectric constant, would cut down considerably the forces of attraction between charges.

(ii) **Polarity :** Water is a polar solvent. As has already been shown that it exists as a liquid at room temperature due to its hydrogen bonding and the dipole-dipole interactions. These interactions play an important role in dissolving electrolytes. When sodium chloride is shaken with excess of water, the solid salt disappears and a solution is formed. There is experimental evidence to believe that sodium and chloride ions are present in combination with water molecules in aqueous solution. Positively charged sodium ions and negatively charged chlo-

ride ions are surrounded by water molecules due to its dipolar character. This is shown in Fig. 2.5 given below :

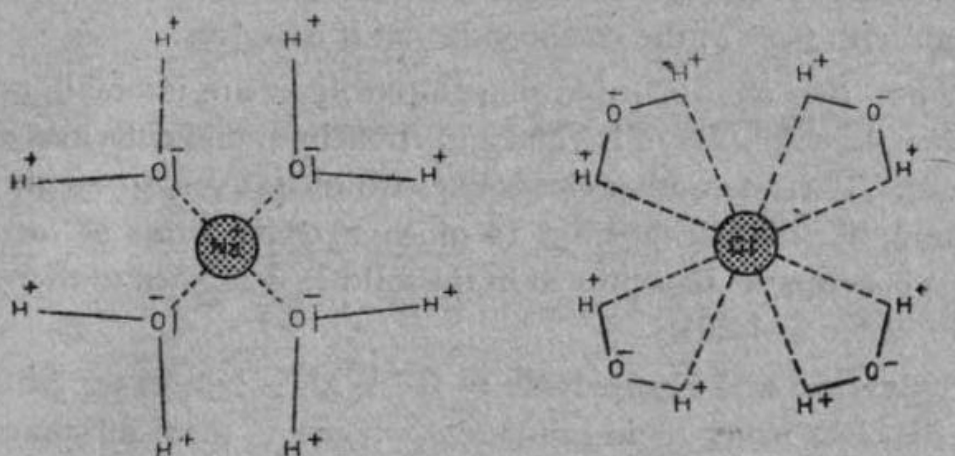
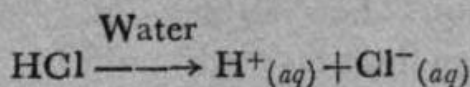


Fig. 2.5

These arrangements of water molecules around positive ions are such that negatively charged oxygens are oriented towards it while for negatively charged ions the opposite is true.

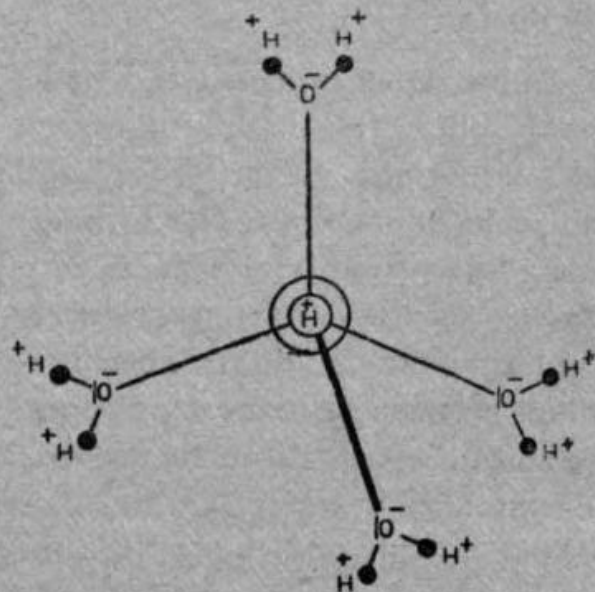
A similar picture is obtained when strong acids are dissolved in water. For example, hydrochloric acid when dissolved in water would split up into protons and chloride ions.



These ions are solvated in a similar fashion as sodium and chloride ions in the previous case. Experiments have shown us that a proton in aqueous solution exists as H_3O^+ , known as hydronium ion. A more accurate picture, however, is when each proton is surrounded by four water molecules tetrahedrally (Fig. 2.6).

Tetrahedral Structure of proton surrounded by four water molecules.

Fig. 2.6



In the end, it may be pointed out that water is not as inactive a solvent as has previously been thought. It has been shown that water interacts with most of the compounds that it dissolves.

It has been observed that some electrolytes are insoluble in water. For example, sulphates of barium and strontium, and chlorides of silver and lead. There are other electrolytes which are very sparingly soluble in water. This is perhaps due to much stronger forces of attraction existing between the ions present in the solid as compared to their attraction for water molecules.

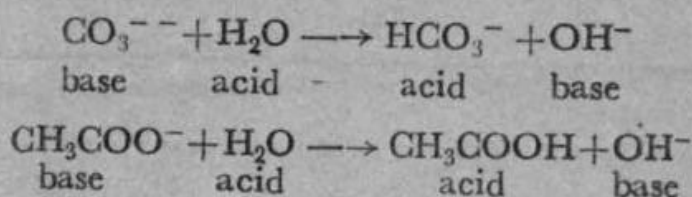
Hydration and Hydrolysis : It has already been explained that water dissolves many ionic substances. Some of these substances may be re-crystallized from water solution with water molecules as part of the crystal lattice. These solid crystalline substances are known as *hydrates*. Some common hydrates are $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$. The amount of water of crystallization may vary from substance to substance. In the above-mentioned examples six, five and two water molecules are present in aluminium chloride, copper sulphate and barium chloride respectively. A small positively charged (Li^+) ion or bigger ion with high charge (Al^{+++} , Ba^{++}) would generally form hydrates. Low charges (Cu^+ , K^+ , Rb^+ , Cs^+) with big volume would not form hydrates easily.

In ionic substances negatively charged ions are generally bigger in size than positive ions. Hence association of water in substances is generally linked with cation rather than with anion. However, in $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ there is experimental reason to believe that at least one water molecule is attached to the sulphate ion and the other four with the Cu^{++} ion.

In hydration process water molecules as such are linked with the crystal lattice. No hydrogen oxygen bonds are broken although new bonds are formed. There is yet another way in which water can react with ionic substances. The hydrogen oxygen bond in water may be broken on reaction with some ionic salts and these reactions are called *hydrolysis reactions*. We may observe that copper sulphate solution in water is acidic, sodium carbonate solution is basic while a solution of sodium chloride is neutral. Copper sulphate and sodium carbonate solutions in water are acidic and basic respectively because these salts are hydrolysed in water.

The hydrolysis reactions may be understood in terms of Bronsted Lowery acid-base theory.

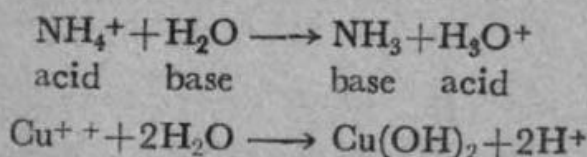
The anions derived from weakest acids are strongly basic. For example, CO_3^{--} , HCO_3^- , S^{--} , CN^- , CH_3COO^- would react with water.



Hence solutions of salts containing these ions will be basic in nature.

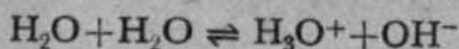
Anions like ClO_4^- , NO_3^- , Cl^- , Br^- , and I^- are so weakly basic that they would not be hydrolysed significantly.

There are strongly acidic cations such as NH_4^+ and Cu^{++} . They would react with water as follows :



Hence their solutions are acidic.

Water as Weak Electrolyte : As has already been said pure water does not conduct electricity but does so if some acid or alkali is added to it. It has been found experimentally, however, that water does show a very small conductivity when a very sensitive instrument is used. This can be explained by saying that water molecules interact to produce charged species.



The above equilibrium can be represented, as

$$K = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]^2} \text{ or } K = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]}$$

$$\text{or } K[\text{H}_2\text{O}] = [\text{H}^+][\text{OH}^-]$$

The concentration of the ions produced is so small as compared to the concentration of water, that the concentration of water remains essentially constant, therefore the term $K[\text{H}_2\text{O}]$ is a constant and is symbolized as K_w . Thus

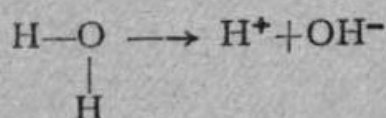
$$K_w = [\text{H}^+][\text{OH}^-]$$

The values of K_w at different temperatures are given in Table 2.2. Its value at 25°C is 1.00×10^{-14} .

Table 2.2

Temperature ($^\circ\text{C}$)		K_w
0	..	0.114×10^{-14}
10	..	0.295×10^{-14}
20	..	0.676×10^{-14}
25	..	1.00×10^{-14}
60	..	9.55×10^{-14}

These values indicate that ionization of water increases with rise in temperature. This is to be expected as bonds in water are broken for ionization.



If it is known that $K_w = 1.00 \times 10^{-14}$, the ionic concentrations for H^+ and OH^- in water at 25°C can be calculated. For example,

$$[\text{H}^+][\text{OH}^-] = K_w.$$

Since the concentration of H^+ equals that of OH^- , we can write

$$[\text{H}^+][\text{H}^+] = [\text{H}^+]^2 = K_w$$

Hence

$$\begin{aligned} [\text{H}^+] &= \sqrt{K_w} \\ &= \sqrt{1.00 \times 10^{-14}} \\ &= 1.00 \times 10^{-7} \end{aligned}$$

For OH^- we may also write

$$[\text{H}^+] = [\text{OH}^-] = 1.00 \times 10^{-7}$$

This result explains the low conductivity of water and since ionic concentrations in water are as low as 1.00×10^{-7} , water may be called a weak electrolyte.

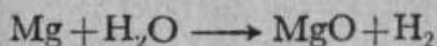
Chemical Reactions of Water : Water reacts with metals like sodium and potassium to yield the respective hydroxides and hydrogen gas. The gas evolved can be tested to be hydrogen, and the liquid gives all the reactions of a base.



The above reaction is highly exothermic and a lot of heat is evolved when sodium or potassium reacts with water.

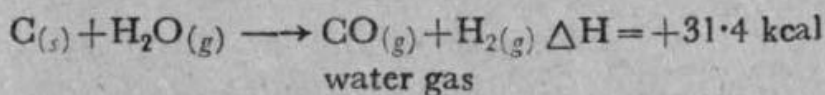
It is found that the reaction of potassium with water is more vigorous than the reaction of sodium, so much so that the hydrogen evolved in the first reaction catches fire.

Magnesium reacts with water much more slowly. A ribbon of Mg is heated and superheated steam is passed over it. The Mg burns brilliantly and MgO is left behind.



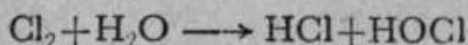
In general metals like Li, Na, K, Rb, Cs, Ca, Sr and Ba react with cold water producing hydrogen gas and the metal hydroxides. On the other hand metals like Be, Mg, Al, Mn, Cr, Fe, Zn and Cd, would not react with cold water. However, these metals react with steam to produce hydrogen gas and the metal oxide.

The reaction of steam with carbon at about 1000°C producing water gas needs special attention. Experiment shows that this reaction is endothermic and when water gas is produced heat is transferred from the surrounding into the system.



The energy stored in water gas is released on burning it. Therefore water gas is a more energetic fuel than coal.

Chlorine reacts with water to produce hydrochloric acid and hypochlorous acid.



Questions

- (a) Water has a dipole moment. Show that this is consistent with the statement that water molecule is not linear.

(b) Give in detail the chemical reactions of water.
- Describe briefly, and step by step the experimental evidence upon which the formula of water *i.e.* H_2O is based.

3. Of alkali metal ions only Li^+ and Na^+ are normally hydrated in ionic solids. On the other hand all the alkaline earth metal ions are normally hydrated under similar conditions as above (room temperature). Explain, why?
4. Classify the following reactions into :
 - (a) hydration reactions, and
 - (b) hydrolysis reactions.
 - (1) $\text{CuSO}_4 + 5\text{H}_2\text{O} \longrightarrow \text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
 - (2) $\text{Zn}^{++} + 4\text{H}_2\text{O} \longrightarrow \text{Zn}(\text{H}_2\text{O})_4^{++}$
 - (3) $\text{PI}_3 + 3\text{H}_2\text{O} \longrightarrow \text{H}_3\text{PO}_3 + 3\text{HI}$
 - (4) $\text{CH}_3\text{COO}^- + \text{H}_2\text{O} \longrightarrow \text{CH}_3\text{COOH} + \text{OH}^-$
 - (5) $\text{H}^+ + 4\text{H}_2\text{O} \longrightarrow \text{H}_9\text{O}_4^+$
5. Calculate the number of moles of water liberated when 24.4 gm. of barium chloride dihydrate is heated? (Answer : 0.2 M).
6. Water gas is made from coal. Why is water gas considered to be more energetic fuel than coal?
7. Water expands when solidified (ice floats on water), explain how this is possible on the basis of the electronic structure of water?
8. Write notes on :
 - (a) Structure of water.
 - (b) Water as a solvent.
 - (c) Water as a weak electrolyte.

Handwritten notes:
 - *Handwritten correction: 5 cm*
 - *Handwritten: Table 1, 2*
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CHAPTER 3

LITHIUM AND BERYLLIUM FAMILIES

Lithium family includes, lithium, sodium, potassium, rubidium cesium and francium. These elements are also known as alkali metals. The name alkali metal for these elements is used because they yield alkaline oxides and hydroxides which neutralize acids in aqueous solutions. Beryllium family consists of beryllium, magnesium, calcium, strontium, barium and radium. Another name for this group is alkaline earth metals. This name is derived from the fact that these metals occur in nature as silicate minerals, and that their oxides and hydroxides like the oxides and hydroxides of alkali metals are alkaline. The properties and electronic configurations of lithium and beryllium groups indicate that there is enough justification in treating the two groups under one chapter. If we look carefully at the crystalline structure, atomic radii, ionic radii, ionization potentials and the behaviour of such compounds as oxides, hydroxides and halides, we gather that lithium and beryllium families have many points in common.

In the following pages some of these properties have been treated in detail to bring out the similarities and the differences between the two groups and the members of these groups more clearly.

The electronic configurations of lithium and beryllium group elements are shown below :

Table 3.1
GROUP I—ALKALI METALS

Element	Symbol	Atomic Number	Electronic Structure
Lithium	Li	3	$1s^2, 2s^1$
Sodium	Na	11	$1s^2, 2s^2p^6, 3s^1$
Potassium	K	19	$1s^2, 2s^2p^6, 3s^2p^6, 4s^1$
Rubidium	Rb	37	$1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6, 5s^1$
Cesium	Cs	55	$1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}, 5s^2p^6, 6s^1$
Francium	Fr	87	$1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}f^{14}, 5s^2p^6d^{10}, 6s^2p^6, 7s^1$

Table 3.2
GROUP II—ALKALI EARTH METALS

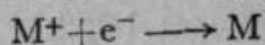
Element	Symbol	Atomic Number	Electronic Structure
Beryllium	Be	4	$1s^2, 2s^2$
Magnesium	Mg	12	$1s^2, 2s^2p^6, 3s^2$
Calcium	Ca	20	$1s^2, 2s^2p^6, 3s^2p^6, 4s^2$
Strontium	Sr	38	$1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6, 5s^2$
Barium	Ba	56	$1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}, 5s^2p^6, 6s$
Radium	Ra	88	$1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}f^{14}, 5s^2p^6d^{10}, 6s^2p^6, 7s$

The metals of lithium and beryllium groups are so reactive that none of them occurs free in nature. Metals of both these groups are strongly electropositive (tendency to lose electrons) and yield positive monovalent and divalent ions, respectively. Only beryllium, with a low atomic volume, behaves differently. It gives many covalent compounds and thus resembles aluminium.

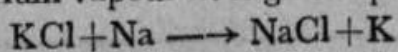
OCCURRENCE AND PREPARATION

The Alkali Metals : Sodium and potassium occur in nature in abundance as salts containing positive monovalent metal ions. Sodium occurs as sodium chloride in salt mines and sea water. Sodium also occurs in nature as part of some minerals (such as zeolites; sodium aluminium silicates), and as sodium nitrate. Potassium is found in nature as potassium chloride and as a double salt, $KCl, MgCl_2, 6H_2O$ (Carnalite). Lithium, rubidium and cesium are comparatively rare.

If alkali metals are to be made from the above-mentioned compounds, a general reaction of the following type is needed :



The above process requires large energy because alkali metals have the tendency to acquire a positive charge. Electrical energy is used for this purpose. Consequently these metals are obtained by the electrolysis of their molten salts. Sodium is prepared by the electrolysis of molten sodium chloride at $850^\circ C$. Other metals are also obtained by a similar method. Potassium is also prepared by reacting molten potassium chloride with sodium vapour at high temperature.

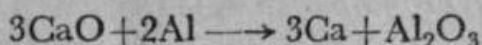


The alkaline earth metals : Beryllium occurs in nature as beryl, ($\text{Be}_3\text{Al}_2\text{Si}_2\text{O}_{18}$). It forms $6 \times 10^{-4}\%$ of the earth's crust. Magnesium is more abundant and makes up to 2% of the earth's crust. Its common ores are asbestos ($\text{CaMg}_3\text{Si}_4\text{O}_{12}$), magnesite (MgCO_3); and dolomite ($\text{MgCO}_3, \text{CaCO}_3$). Magnesium salts also occur in sea water. Calcium is found as CaCO_3 (lime stone, marble, chalk), and $\text{CaSO}_4 \cdot \text{H}_2\text{O}$ (gypsum). Calcium salts occur abundantly in nature. As a matter of fact this is the most abundant of all the elements of lithium and beryllium groups. Strontium occurs as SrCO_3 (Strontionite), and barium as BaSO_4 (Barytes). These ores, however, are comparatively rare.

The preparation of alkaline earth metals involves the reduction of divalent metal ions. This can either be done through electrolysis or by using reducing agents.

Beryllium is obtained by reducing BeF_2 with magnesium at elevated temperatures. It can also be obtained by the electrolysis of a molten mixture of BeCl_2 and NaCl .

Magnesium is generally prepared by electrolysis of molten MgCl_2 . H_2O . Calcium, barium, and strontium metals are obtained by the electrolysis of their molten chlorides containing some sodium chloride. Another important method for the preparation of these metals involves the reaction of their oxides ($\text{CaO}, \text{SrO}, \text{BaO}$) with aluminium at high temperature. The reactions are so exothermic that the calcium, barium and strontium metals distil over from the reaction mixture.



All the alkali metals are extremely reactive, tarnishing immediately upon exposure to air. For this reason they are usually stored in vacuum sealed containers or under kerosene or mineral oil. Their general reaction with water may be given by the following equation in which "M" stands for any of the alkali metals :



The reaction becomes progressively more energetic from Li to Cs. The alkali metals all burn in air or oxygen, Li gives Li_2O , Na gives primarily Na_2O_2 , and K, Rb, and Cs give the superoxides, e.g., KO_2 . In all these compounds the alkali metals exhibit an oxidation number of +1.

PROPERTIES

Ist Group elements : The alkali metals are all silvery, lustrous metals with low melting points. They conduct heat and electricity

easily. Some of their important properties are listed in the Table (3.3) below :

Table 3.3
IMPORTANT PROPERTIES OF GROUP I
ELEMENTS

	Li	Na	K	Rb	Cs
Ionization energy	124	118	100	96	90
Atomic radius	1.33	1.57	2.03	2.16	2.35
Melting point °K	454	371	336	312	302
Boiling point °K	1640	1163	1040	970	958
ΔH_{sub} kcal mole ⁻¹	38.4	25.9	21.5	19.5	18.7
Ionic radius	0.68	0.98	1.33	1.48	1.67
ΔH_{hyd} kcal mole ⁻¹	121	95	76	69	62

The trend in the melting and boiling points of these metals indicates that as the atomic number increases the melting and boiling points decrease. It probably means weaker interactions among metal atoms in the crystal lattice. This fact is observed in Lithium metal which is difficult to cut with a blunt knife. Sodium, potassium, rubidium and cesium are easier to cut (soft) in that order. The trend of the values of ΔH also confirms this idea. It may be noted that a decreasing value of ΔH_{sub} from Li to Cs means that the energy required to gasify these metals decreases in that order. The first row in the above table gives the values for the ionization energies for these metals. This is the energy which must be spent to remove one electron from metal atoms to yield Li^+ , Na^+ , K^+ , Rb^+ , and Cs^+ . The value of ionization energy decreases with rise in atomic number, meaning that the electropositivity increases from Li to Cs. In the last row of the table are given values for the heat of hydration for the above ions. These values of ΔH_{hyd} in kcal indicate the amount of heat generated when a mole of such ions goes into the aqueous solution. Note that as the ionic radii increase, the ΔH_{hyd} decreases. This means that Li^+ has the positive charge concentrated on a smaller volume relative to Cs^+ , where the charge rests on a bigger volume and hence is more diffused. Therefore, interaction between Li^+ and water is stronger than the interaction between Cs^+ and water. This trend is beautifully shown by the values of ΔH_{hyd} given in the above table.

Because of their low ionization energies, the alkali metals, especially Cesium, find use in photocells. When light shines on metals like cesium (or other metals coated with it), electrons from the metal surface are easily emitted and this principle (Photoelectric Effect) helps in making television pick up devices.

The salts of the alkali metals are colourless, unless the anion with which the alkali metal is associated happens to be coloured, *e.g.*, permanganate or chromate. They are crystalline compounds and with few exceptions are soluble in water. Their solubility is related to their ionic radii. Large positive ions of K and Rb are more soluble in water than Li ions. Thus phosphate and carbonate of Li are insoluble in water. All the alkali metal bicarbonates are soluble in water.

II Group elements : The metals of Group II are harder than metals of Group I. However, the trend of increasing softness like Group I is present in this group also. Magnesium is useful for its structural properties. When mixed with aluminium, zinc, or manganese, magnesium finds extensive use in aircrafts and rail road industries because it yields light and strong alloys.

The greater hardness in Group II as compared to Group I suggests that interactions between metal atoms in Group II are stronger than in Group I.

Melting points, boiling points and heats of ionization for alkaline earth metals along with other properties are given in the Table 3.4.

Table 3.4

	Be	Mg	Ca	Sr	Ba
Ionization energy					
ΔH_1	214	175	140	132	120
ΔH_2	429	345	274	253	230
Atomic radius	0.89	1.36	1.74	1.91	1.98
Melting point °K	1556	929	1123	1043	983
Boiling point °K	2700	1400	1750	1640	1950
ΔH_{sub} kcal mole ⁻¹	77.9	35.6	42.2	39.1	42.5
Ionic radii	0.30	0.65	0.94	1.10	1.29
ΔH_{hyd} kcal mole ⁻¹	570	460	395	355	305

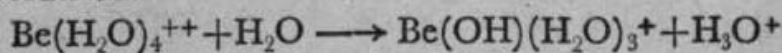
The above table shows that the atomic and ionic radii for these metals increase from Be to Ba. When the values of atomic and ionic radii of the metals of group II are compared with the values of the group I, it is found that the radii (particularly ionic radii) are much smaller for group II than for group I. Note that Li^+ and Be^{++} , Na^+ and Mg^{++} , and K^+ and Ca^{++} are isoelectronic (containing same number of electrons) but each alkaline earth ion has a bigger charge than their alkali ion partner and this explains the decrease in ionic size from alkali to alkaline earth metals.

Like the ΔH_{hyd} of group I ions, the values of ΔH_{hyd} for group II ions (Be^{++} , Mg^{++} , Ca^{++} , Sr^{++} and Ba^{++}) decrease with rising atomic number. However, the ΔH_{hyd} values for alkaline earth metal ions are much greater than those of alkali metal ions. This can be explained in terms of greater charge density on divalent alkaline earth metal ions as compared to the monovalent alkali metal ions. It is noted that Na^+ and Ca^{++} have nearly the same ionic radii but ΔH_{hyd} value of Ca^{++} is almost four times as that of Na^+ .

COMPOUNDS AND REACTIONS

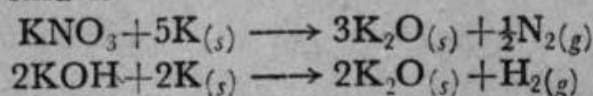
Most of the compounds of the alkali and alkaline earth metals are ionic in nature. They are colourless and diamagnetic solids. Lithium and beryllium also form compounds which show covalent characteristics. The alkali metal compounds are soluble in water and their solubility is related to their ionic radii. Large positive ions of K and Rb are more soluble in water than the smaller lithium ions. The solubilities of lithium salts are generally similar to those of magnesium salts. The phosphates, carbonates and fluorides of all the alkali metals are soluble except those of lithium.

The metal ions of alkali and alkaline earth metals are not hydrolysed in water and thus exhibit weak acidic properties. Lithium, beryllium and magnesium ions are, however, somewhat hydrolysed and yield acidic solutions.

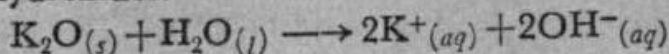


Group I—Oxides and Hydroxides : Direct burning of alkali-metals in oxygen yields various types of oxides. Lithium gives a normal oxide of the formula Li_2O , while sodium gives sodium peroxide, Na_2O_2 . Other alkali metals give superoxides of the formula MO_2 .

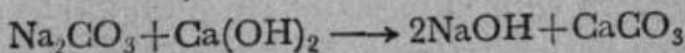
Simple oxides of these metals can be obtained by reduction of their nitrates and hydroxides.



These oxides are ionic in nature and dissolve readily in water to give the respective hydroxides.



Sodium hydroxide can also be obtained by the above reaction. On the industrial scale, sodium hydroxide is obtained by mixing sodium carbonate with calcium hydroxide as a slurry.

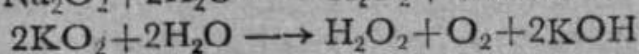


Calcium carbonate is precipitated and can be easily removed.

Sodium hydroxide is also obtained as by-product in the electrolysis of brine (aqueous sodium chloride) in a special kind of cell (see Chapter on Halogens). Potassium hydroxide can be prepared by the above-mentioned methods. For instance a reaction between barium hydroxide and potassium sulphate yields potassium hydroxide.

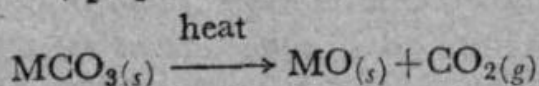
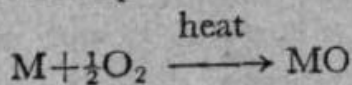


Potassium superoxide (KO_2) and sodium peroxide (Na_2O_2) are compounds of industrial importance because of their oxidizing properties. They are also important because of their reactions with water to give hydrogen peroxide.



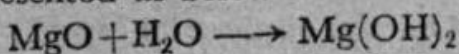
Group II Oxides and Hydroxides : Alkaline earth metal oxides are prepared by :

- (1) heating the metal in oxygen, and
- (2) thermal decomposition of carbonates.



Here M stands for Mg, Ca, Sr, Ba, etc.

These oxides are ionic solids with high melting points. They all react with water to give metal hydroxides. Beryllium oxide is exceptionally unreactive towards water. The reaction between magnesium oxide and water is slow. Calcium, strontium and barium oxides react with water more vigorously and their reactivity increases in the above-mentioned order. The reactions are exothermic and may be represented as below :



$$\Delta H = -5.4 \text{ kcal/mole}$$

$$\Delta H = -15.1 \text{ kcal/mole}$$

$$\Delta H = -17.7 \text{ kcal/mole}$$

$$\Delta H = -22.3 \text{ kcal/mole}$$

It is clear from the above reactions that oxides of Mg, Ca, Sr and Ba are strongly basic. The properties of beryllium oxide are, however, different. It is acidic as well as basic in nature and is, therefore, said to be *amphoteric*.

Diagonal Relationship : Elements of the 2nd period show a diagonal relationship with elements of 3rd period. For example Li, Be and B of the 2nd period resemble Mg, Al and Si of the third period respectively :

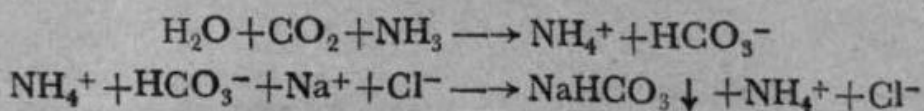
Groups	I-A	II-A	III-A	IV-A
2nd period	Li	Be	B	C
3rd period	Na	Mg	Al	Si

Li in group I-A is more electropositive than Be in group II-A, but Mg is also more electropositive than Be. Thus both Li and Mg are more electropositive than Be and less electropositive than Na. So far as the sizes of ions are concerned, Li^+ ion is almost of the same size as Mg^{+2} ion. Similarly Be^{+2} and Al^{+3} ions have approximately the same ionic size. In the aqueous medium both the Be^{+2} and Al^{+3} ions become heavily hydrated and they act as a good proton donor. The hydroxides of Be and Al show both acidic as well as basic reactions. Both the chlorides of Be and Al are more covalent than ionic in nature. These salts have comparatively low melting points (405°C and 193° respectively), than the chlorides of the other members of their respective groups. In molten state these salts are poor conductors of electricity. Be reacts, with NaOH similar to Al, to form BeO_2^- and AlO_2^- ions respectively. BeO and Al_2O_3 both have high melting points.

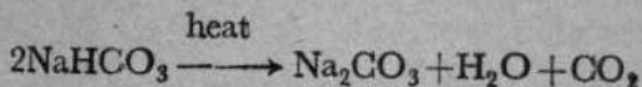
CARBONATES AND BICARBONATES

Lithium and beryllium families form compounds of the type M_2CO_3 , MHCO_3 where M stands for Li, Na, K, Rb, or Cs and MCO_3 , $\text{M}(\text{HCO}_3)_2$ where M represents metals of the alkaline earth group. The most common and useful carbonates and bicarbonates are those of sodium (Na_2CO_3 and NaHCO_3). On the industrial scale these compounds are prepared by the *Ammonia Solvay* process. In this process ammonia and carbon dioxide are passed under pressure through a NaCl solution at 15°C .

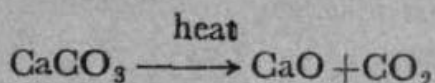
The reactions taking place for the production of bicarbonate may be represented as :



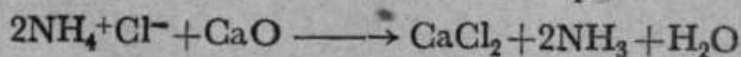
At a temperature as low as 15°C and due to higher concentration of Na^+ in solution, a precipitate of sodium bicarbonate is obtained. This is filtered off, dried and heated to get sodium carbonate.



The carbon dioxide evolved in the above reaction is used to obtain more sodium bicarbonate. The solution containing NH_4^+Cl^- is heated with CaO obtained from calcium carbonate :

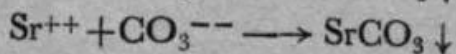
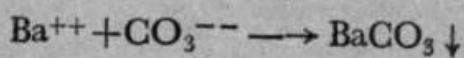


to evolve ammonia which is used in the first step.

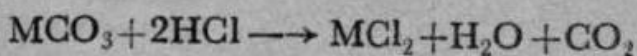


Anhydrous sodium carbonate is known as soda ash. It also exists as a decahydrate, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, known as washing soda. Soda ash finds extensive use in glass and soap manufacture. All the alkali metal carbonates except lithium are very soluble in water. Sodium bicarbonate is commonly used in baking bread, etc. and hence is known as baking soda. All the alkali metal bicarbonates are soluble in water. They are easily decomposed on heating to the corresponding carbonates, water and carbon dioxide.

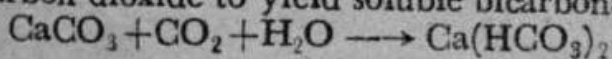
The carbonates of alkaline earth metals unlike the carbonates of alkali metals are insoluble in water. They can be prepared by bringing together in solution alkaline earth metal ion and CO_3^{--} ion.



All the carbonates, including the carbonates of group II evolve carbon dioxide on reaction with acids.



The carbonates of alkaline earth metals dissolve in water containing dissolved carbon dioxide to yield soluble bicarbonates.



Questions

1. Account for the following facts :
 - (a) Sodium forms $+1$ ions but not $+2$ ions.
 - (b) Decrease in hardness, melting and boiling points down the alkali-metal group.
 - (c) Li^+ has much higher value of heat of hydration than Cs^+ .
 2. Give balanced equations for the following reaction :
 - (a) Potassium with water.
 - (b) Heating alkali metal in oxygen.
 - (c) Calcium oxide with water.
 - (d) Alkali metal carbonates with acids.
 3. Show, with equations, the various steps in the preparation of sodium carbonate by the Solvay process.
 4. In what respects is beryllium more similar to aluminium than to the members of its own family?
 5. Write equations for the reactions which occur when Mg is burned in air and the products are treated with water.
 6. What are the chief differences between the properties of the alkali metal compounds and those of the alkaline earth metals.
-

CHAPTER 4

Group III

BORON AND ALUMINIUM

Group III elements are related to group II elements in very much the same way as the group II elements are related to those of group I. Their electronic configurations suggest that an addition of one more electron in the valence shell of the second group configuration would yield electronic structures for atoms of the group III elements. This argument can be taken further to say that group III elements would show horizontal relationship with group II elements. They would also show periodic relationship among themselves because of their similar electronic structures. This kind of relationship in fact is observed when we look at some of the properties given in tables 4.1 and 4.2.

Table 4.1

PROPERTIES OF GROUP III ELEMENTS

Property	Boron	Aluminium	Gallium	Indium	Thallium
Atomic number ..	5	13	31	49	81
Atomic weight ..	10.82	26.97	69.72	114.76	204.39
M. P. °C ..	2300	658	29.75	155	303.5
B. P. °C ..	2550	1800	1700	1450	1650
Atomic radius A° ..	0.80	1.25	1.25	1.50	1.55
Ionic radius A° ..	0.20	0.52	0.60	0.81	0.95
Electronegativity ..	2.0	1.5	1.6	1.7	1.8

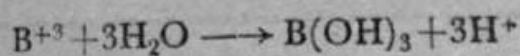
Table 4.2

Element	Symbol	At. No.	Electronic configuration
Boron	B	5	$1s^2, 2s^2p^1$
Aluminium	Al	13	$1s^2, 2s^2p^6, 3s^2p^1$
Gallium	Ga	31	$1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^1$
Indium	In	49	$1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}, 5s^2p^1$
Thallium	Tl	81	$1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}f^{14}, 5s^2p^6d^{10}, 6s^2p^1$

Boron is a semimetal. It is similar to Li and Be of the groups I and II respectively. The peculiarity in properties of Li, Be and boron as compared to the subsequent elements of these groups may be explained by realizing that these elements have electronic configurations in which valence electrons are shielded from the nucleus only by K shells. Like lithium and beryllium, boron also has small atomic size. This gives boron a higher ionization potential than aluminium, gallium, indium and thallium. Because of its high ionization potential boron is less metallic than the other elements of this group.

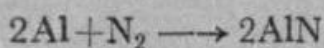
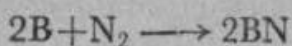
From the electronic configurations of these elements, we might expect that M^{+3} ions, may be formed. However, boron due to its low atomic size (strong hold on its electrons), does not yield B^{+3} and enters into chemical combinations by making covalent bonds. Other elements of this group lose electrons to give M^{+3} ion and the ease of formation of such ions increases down the group.

The acidic character in this group decreases with rise in the atomic number. Boron yields acidic oxides and hydroxides. Aluminium and gallium give amphoteric oxides and hydroxides, while such compounds for indium and thallium are basic, thus revealing their metallic character. This can be explained by assuming that the sizes of B^{+3} , Al^{+3} , Ga^{+3} , In^{+3} and Tl^{+3} increase in that order. B^{+3} , when placed in water, due to its smaller size would attract the electrons of water giving $B(OH)_3$. This would make B_2O_3 acidic.

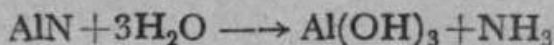
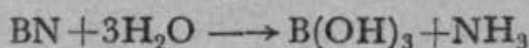


Al^{+3} and Ga^{+3} are larger than B^{+3} and hence hydrolyse to a lesser extent. Therefore, Al_2O_3 and $\text{Al}(\text{OH})_3$ are amphoteric. In^{+3} and Ga^{+3} are not hydrolysed in water because the size of their ions is too big to disturb the electron clouds on water molecule.

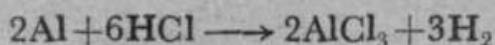
B, Al and other metals of this group form nitrides when strongly heated with nitrogen.



These nitrides react with water forming NH_3 and the corresponding hydroxides.

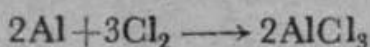
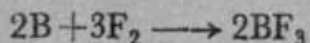


Boron does not react with dilute acids, but Al and other metals of group III react, liberating hydrogen.



Strong HNO_3 and H_2SO_4 , however oxidize boron to boric acid H_3BO_3 . Boron is not effected by dilute alkali, but in hot concentrated alkali it may form alkali borate. Al reacts with alkali to form aluminate and hydrogen.

Boron and Al react with halogens forming the corresponding halides.



Boron differs from Aluminium in certain respects. For example Al is a typical metal, whereas B is a non-metal and exists in amorphous and crystalline varieties. The oxide of boron (B_2O_3) is acidic in nature, whereas Al_2O_3 is amphoteric. Boron forms stable hydrides of covalent nature i.e., B_2H_6 , B_4H_{10} , but Al does not form stable hydrides. Boron has a capacity to form acids like H_3BO_3 , (ortho-boric acid), HBO_2 (metaboric acid), $\text{H}_2\text{B}_4\text{O}_7$ (tetra boric acid), but Al does not form such acids.

BORON

OCCURRENCE

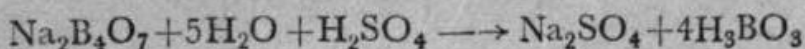
Boron is a rare element and is present in earth's crust to the extent of about 0.001%. It mainly occurs as ortho-boric acid (H_3BO_3) and as borax $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$.

Boron is a poor conductor of electricity and possesses a dull metallic luster. It is hard and brittle. It is not classified as a metal. However, when boron is heated, its properties change; especially its conductivity increases rapidly with temperature. For this reason boron with other substances like silicon and germanium is called a semiconductor. The explanation of the semi-conductivity may be given in terms of the tightly bonded electrons in the crystal lattice of boron which, are freed from their lattices at higher temperatures and wander around in the crystal to make the substance a good conductor of electricity.

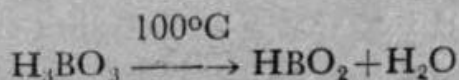
At room temperature boron is almost inert and is only attacked by extremely strong oxidizing agents such as concentrated nitric acid and fluorine. It forms borates when fused with NaNO_3 and NaOH . Some of the compounds of boron are discussed in the following pages.

BORIC OXIDE, BORIC ACID AND BORATES

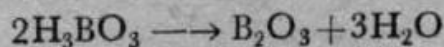
Boric oxide, B_2O_3 , is a colourless compound. Its melting point is 557°C , and boiling point 1500°C . The considerably higher values of melting and boiling points of B_2O_3 indicate that the compound probably exists as aggregates rather than simple molecules. Boric oxide is soluble in hot water to the extent of 15.7 grams per 100 ml of H_2O at 100°C . The hot aqueous solution of B_2O_3 yields a white crystalline compound H_3BO_3 (ortho boric acid) on cooling. This substance is commercially known as boric acid and can be prepared by acidification of an aqueous solution of borax.



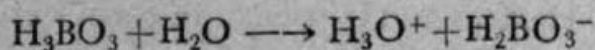
Ortho boric acid can be dehydrated on heating to yield B_2O_3 . But under controlled conditions of temperature H_3BO_3 gives other intermediate products. At 100°C , H_3BO_3 loses a water molecule giving of meta boric acid :



The reaction of B_2O_3 formation is



Of all these acids, only boric acid H_3BO_3 , can be isolated from aqueous solution. In aqueous solution it behaves as a very weak acid. The only stage of its ionization large enough to be measured is the first one,

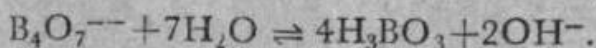


and this has an ionization constant of about 6×10^{-10} mole/litre at 25°C .

The important salt of boric acid is borax and it can be prepared by neutralizing ortho boric acid with a strong base. Borax is a tetraborate and not an ortho borate as should be expected by this reaction.

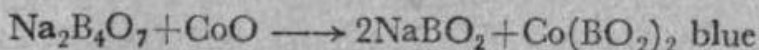


The salt crystallizes from aqueous solution as $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$. As a result of hydrolysis of borate ion, the aqueous solutions of the salt are alkaline in reaction:



The compound is used in softening of water and in the manufacture of borate glass. Borate glasses are heat resisting and are therefore used in the manufacture of laboratory glassware.

The salts of metaboric acid (HBO_2) can be prepared by fusion of sodium tetraborate with metal oxides. The meta borates have glassy appearance and are usually associated with characteristic colours depending upon the nature of the metal oxide involved, *e.g.* cobalt oxide gives a blue glass due to the formation of cobaltmeta borate.



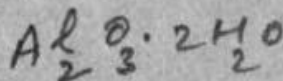
This reaction is utilized in "borax bead test" for the identification of certain metal ions in qualitative inorganic analysis.

ALUMINIUM

OCCURRENCE

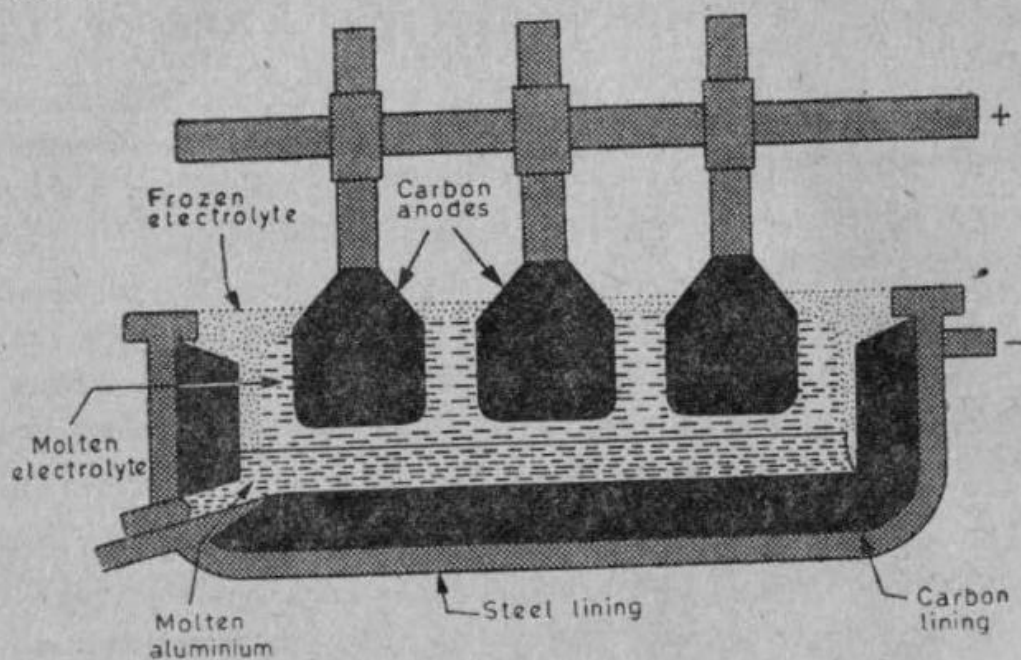
Aluminium is the third most abundant element in the earth's crust (about 7.5%). It does not occur in the free state. In combined form it is found in a variety of minerals like clays and soils. Its important ores are bauxite ($\text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O}$) and cryolite (Na_3AlF_6).

EXTRACTION OF ALUMINIUM



Aluminium is obtained from bauxite (Al_2O_3) by electrolytic reduction. The process is called Hall-Beroult Process. Alumina is dissolved in fused cryolite (Na_3AlF_6). The molten mixture is electrolysed in a steel tank lined with graphite which serves as cathode. The anodes made up of carbon rods are suspended in molten solution. The electrolysis is carried out at a temperature of 900-1000°C. During the process of electrolysis some AlF_3 is considered to be formed from the solution of Al_2O_3 in fused cryolite, Na_3AlF_6 . This on electrolysis yields alumi-

nium metal at the cathode, in molten state which collects at the bottom of the cell.



Extraction of Aluminium

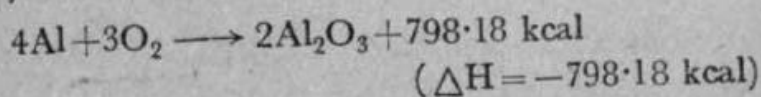
Fig. 4.1

PROPERTIES OF ALUMINIUM

Silvery white aluminium has a very low density (2.70 g/ml.). The pure aluminium is soft and weak, but its strength can be increased considerably by alloying with metals like Cu or Mg. The pure metal is an excellent conductor of heat and electricity.

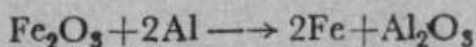
Although the metal is very reactive, aluminium does not corrode in air nor it is effected by water, even at high temperatures. The considerable resistance to corrosion arises from the fact that a thin film of adherent oxide is formed over the surface of the metal. The oxide film serves as a protective coating and inhibits further attack.

Aluminium reacts with oxygen at high temperature and the reaction is strongly exothermic.

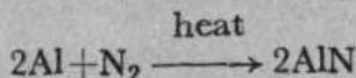
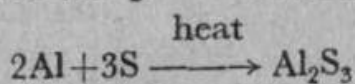
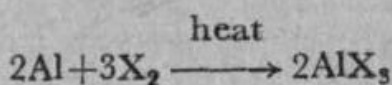


Because of the high heat of formation of Al_2O_3 , as indicated by the above reaction, aluminium powder can be used as a powerful reducing agent for many metal oxides. So much heat is liberated in these reactions that the reduced metal is obtained in the molten condition. The reduction of metal oxides involving aluminium as a reducing agent is termed as *thermite process*. Aluminium burns in oxygen and forms Al_2O_3 ,

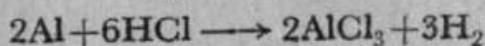
with the evolution of large amount of heat (798 kcal). This heat produced is sufficient to melt the metal. The oxides of other metals like Fe_2O_3 , Cr_2O_3 , Mn_2O_3 , which are ordinarily not possible to be reduced by other methods, are reduced by aluminium to the metallic state in this process *e.g.*,



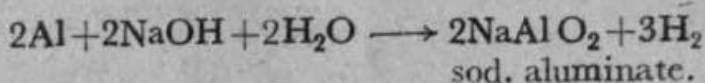
Aluminium reacts with halogens to yield trihalides; with sulphur it yields a sulphide (Al_2S_3), and with nitrogen it gives a nitride (AlN).



Aluminium reacts with aqueous solutions of strong acids such as hydrochloric acid and sulphuric acid with the liberation of hydrogen. In concentrated nitric acid aluminium forms a protective oxide film on the metal surface and becomes passive.



Aluminium also reacts with solutions of strong alkalis forming aluminates with the evolution of hydrogen.

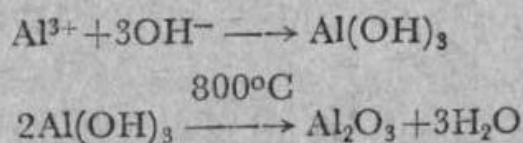


OXIDES OF ALUMINIUM

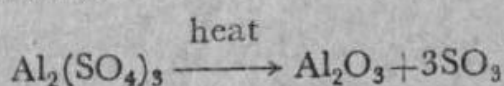
A variety of aluminium oxides occur in nature. Pure anhydrous aluminium oxide exists as corundum (Al_2O_3). It is very hard and chemically inert. Because of these properties it is used as an abrasive and refractory material. If other metal oxides are present as impurities, corundum acquires different colours. These coloured deposits of corundum are used as gem stones, *e.g.*, ruby, sapphire amethyst, etc. Now-a-days all these are synthetically produced and are used as bearings (jewels) in watches and other instruments. Bauxite ($\text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O}$) is a naturally occurring hydrated oxide and is used for extraction of aluminium metal.

When an aqueous solution of aluminium salt is treated with a weak base like ammonia solution, a white gelatinous compound is precipitated.

This precipitate contains indefinite amount of water molecules and is termed as hydrated aluminium oxide. The compound is also called aluminium hydroxide and is assigned the formula $\text{Al}(\text{OH})_3$, but a more correct representation is $\text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O}$. On heating to a temperature of about 800°C the hydrated oxide yields anhydrous aluminium oxide.



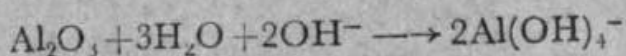
Pure aluminium oxide can also be prepared by ignition of aluminium sulphate or an alum.



Both anhydrous and hydrated aluminium oxides are amphoteric and are thus capable of exhibiting weakly basic and weakly acidic behaviour. They dissolve in solutions of both strong acids and strong bases. Reaction with acids gives Al^{3+} ions in solution.



The reaction with strong bases gives rise to the formation of aluminate ion, $\text{Al}(\text{OH})_4^-$:



When hydrated aluminium oxide is heated above a temperature of 1000°C , it undergoes undefined changes to give an anhydrous substance having the properties of corundum. Commercial bauxite is converted to an inert oxide by igniting it to a temperature of 3000°C . This synthetic material is called alundum and, like corundum, is used as a refractory material and abrasive.

Finely divided aluminium oxide called activated alumina is used as a catalyst, as a dehydrating agent, and in chromatography.

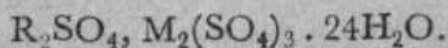
ALUMINIUM SALTS AND ALUMS

The most important compound of aluminium which is widely used is aluminium sulphate. The salt is prepared directly from bauxite by treating it with H_2SO_4 :



The solutions containing equimolecular proportions of $\text{Al}_2(\text{SO}_4)_3$ and K_2SO_4 on evaporation yield a crystalline double salt of the composition, $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$. This compound is known as alum.

Since Potassium and Aluminium can be replaced by other metals of the same valencies, so an alum is now referred to a class of isomorphous, double sulphate of the general formula,



Where R is an atom of mono-valent metal or radical such as Na, K, Rb, Cr, Ag, NH_4 etc., and M is a trivalent metal like Al, Fe(ic), Cr etc. Some important examples are :

Potash or common alum $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$

Ferric alum $(NH_4)_2SO_4 \cdot Fe_2(SO_4)_3 \cdot 24H_2O$

Chrome alum $K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24H_2O$

Alums are converted to a porous mass on strong heating.

Alums are examples of compounds containing mixed crystals and have no complex ions.

Aluminium sulphate and alum are widely used in dyeing linen and cotton cloth. Al^{3+} ions of these salts are precipitated on the cloth as gelatinous $Al(OH)_3$ in presence of a dye. $Al(OH)_3$ has a greater tendency for absorption of the dye and fixes it firmly to the fabric. The process is called *mordanting*, and the aluminium salt is called a *mordant*. Other hydrated gelatinous oxides can also be used as mordants.

Alum can also be used for the purification of water, coagulation of colloidal substances, tanning of hides and sizing of paper.

Questions

1. What electronic configuration do the elements of the boron-aluminium family exhibit in their outer most (valence) shell?
2. What is most significant difference between boron and the other members of the boron-aluminium family?
3. Write equations to show how the following changes can be effected :
 - (a) $H_3BO_3 \longrightarrow B_2O_3$
 - (b) $H_3BO_3 \longrightarrow Na_2B_4O_7 \longrightarrow Co(BO_2)_2$
 - (c) $Al \longrightarrow Al^{3+} \longrightarrow Al(OH)_3 \longrightarrow Al^{3+}$
4. What is an alum? Describe the chief uses of Potash alum. What chemical and physical properties does alum exhibit?

5. Contrast the chemical behaviour of the following pairs :
 - (a) B and Al
 - (b) B and Li
 6. Explain the decrease of acidic character of the elements with rise in atomic number.
 7. In what ways is boron similar to Li and Be in its properties?
 8. What is a thermite process? Give its uses.
 9. What is the composition of borax and to what class of salts does it belong? What is the action of a solution of borax on litmus? Give its uses.
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CHAPTER 5

Group IV

CARBON AND SILICON

The elements of Group IV of the Periodic Table are carbon (C), silicon (Si), germanium (Ge), tin (Sn), and lead (Pb). The symbols for tin and lead are derived from their Latin names, stannum and plumbum.

The electronic configurations of the elements of this group are given in Table 5.1.

Table 5.1

ELECTRONIC CONFIGURATIONS OF GROUP IV ELEMENTS

Valence

Element	Symbol	Z	ELECTRONIC CONFIGURATION	
			Kernel	X Outermost shell
Carbon	C	6	$1s^2$	$2s^2 2p^2$
Silicon	Si	14	$1s^2 2s^2 2p^6$	$3s^2 3p^2$
Germanium	Ge	32	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$	$4s^2 4p^2$
Tin	Sn	50	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$ $4s^2 4p^6 4d^{10}$	$5s^2 5p^2$
Lead	Pb	82	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$ $4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10}$	$6s^2 6p^2$

Valence

It is seen that in each case the ~~X~~ outermost shell has a total of four electrons, two in an s orbital and two in p orbitals. In each case the element will either lose four electrons or gain four electrons to complete its octet. Carbon and silicon do not form ionic bonds either by losing or gaining four electrons. Instead they share their outer

electrons with other elements to complete their octets and form covalently bonded compounds. Tin and lead, however, have a tendency to form ionic bonds by losing their outer electrons. In this they resemble other electropositive elements (metals).

OCCURRENCE

Carbon : Carbon occurs both in the free state and in the form of its compounds.

In the free state it occurs in the form of diamond, graphite and coal. Diamond and graphite are highly pure forms of carbon, whereas coal is an impure form. In Pakistan coal deposits are found at Dandot. In the combined state carbon occurs in natural gas, petroleum, plants, animals, mineral carbonates such as limestone, dolomite, and chalk, and carbon dioxide present in air.

Silicon : Silicon is found abundantly on earth and constitutes about 26% of the earth's crust. It does not occur free in nature. Combined with oxygen, it is found in sand, flint, quartz and opal, all having the formula SiO_2 . In more complex forms it occurs in all rocks, clays and soils.

Germanium, Tin and Lead : Germanium is less common. The more common mineral of tin is cassiterite, SnO_2 , and that of lead is galena, PbS .

SOLID STATE OF THE ELEMENTS

Carbon : Diamond, coal, charcoal, and lampblack, etc. are the solid forms of carbon. Diamond and graphite are the two allotropic modifications of carbon. Coal, charcoal and other forms of carbon have structures resembling graphite, although these structures are imperfect.

Diamond : Diamond is probably the hardest substance known. In its purest form, diamond is colourless; the presence of any colour is due to impurities. It is a very bad conductor of electricity and has a very high melting point.

An important characteristic of diamond is its high refractive index, 2.45. The light entering diamond gets bent strongly from its otherwise straight path, and is reflected off the internal surfaces. The brilliance of diamond is due to such internal reflections. By suitably cutting the diamond the internal reflection surfaces can be increased.

Diamonds are used as precious stones. Inferior quality diamonds are used in rock drilling tools and for cutting glass.

Graphite : Graphite is grey in colour with a dull metallic lustre and is very soft. Due to its softness it is used as a lubricant. It is also used in making lead pencils. Graphite, unlike diamond is a very good conductor of electricity. Graphite has a high melting point. It is less dense (2.25 g/cc) as compared to diamond (3.51 g/cc), but it is the more stable form. At ordinary temperatures diamond should change to graphite. This change however, is infinitely slow. At high temperature and pressure diamond is more stable than graphite. This is in accordance with Le Chatelier's principle—at high pressure the denser form, diamond, should be favoured.

Structure of Diamond and Graphite : In nature elemental carbon is found in two different crystalline forms, namely, graphite and diamond. Graphite and diamond are two different substances and their physical properties are listed below :

	<i>Graphite</i>	<i>Diamond</i>
Colour	greyish black	colourless
Crystal form	hexagonal plates	cubic
Hardness	soft	hardest natural substance known
Density at 20°C	2.26 g/ml	3.51 g/ml

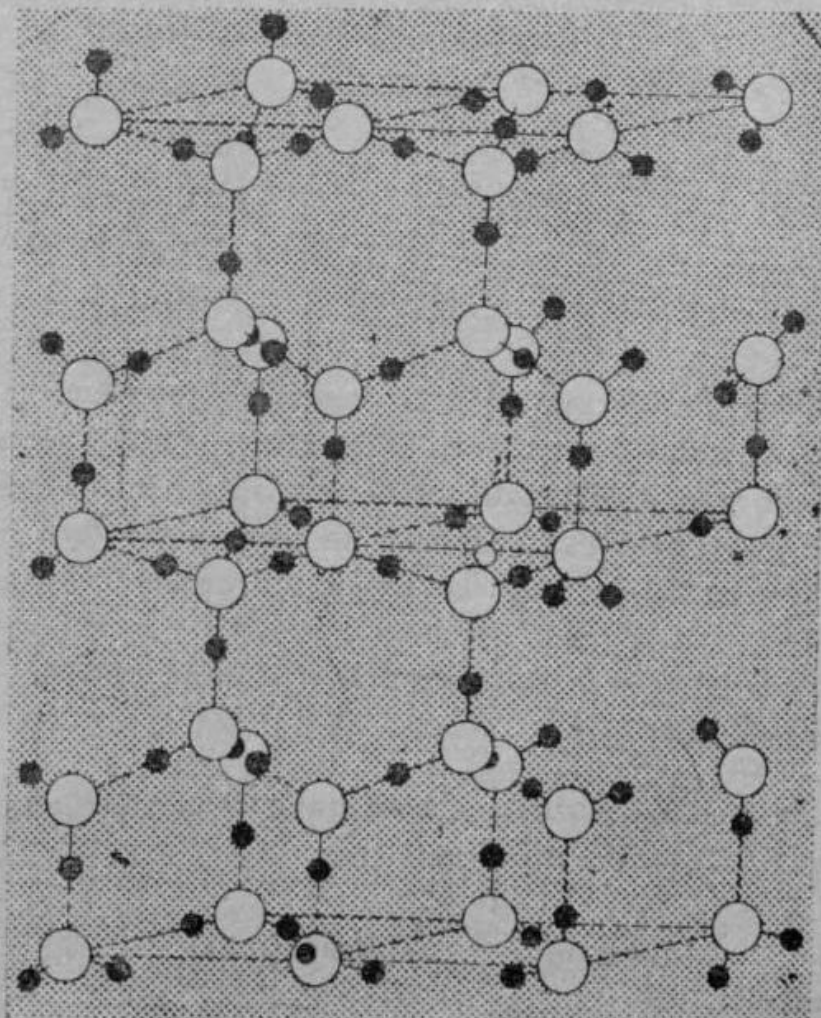
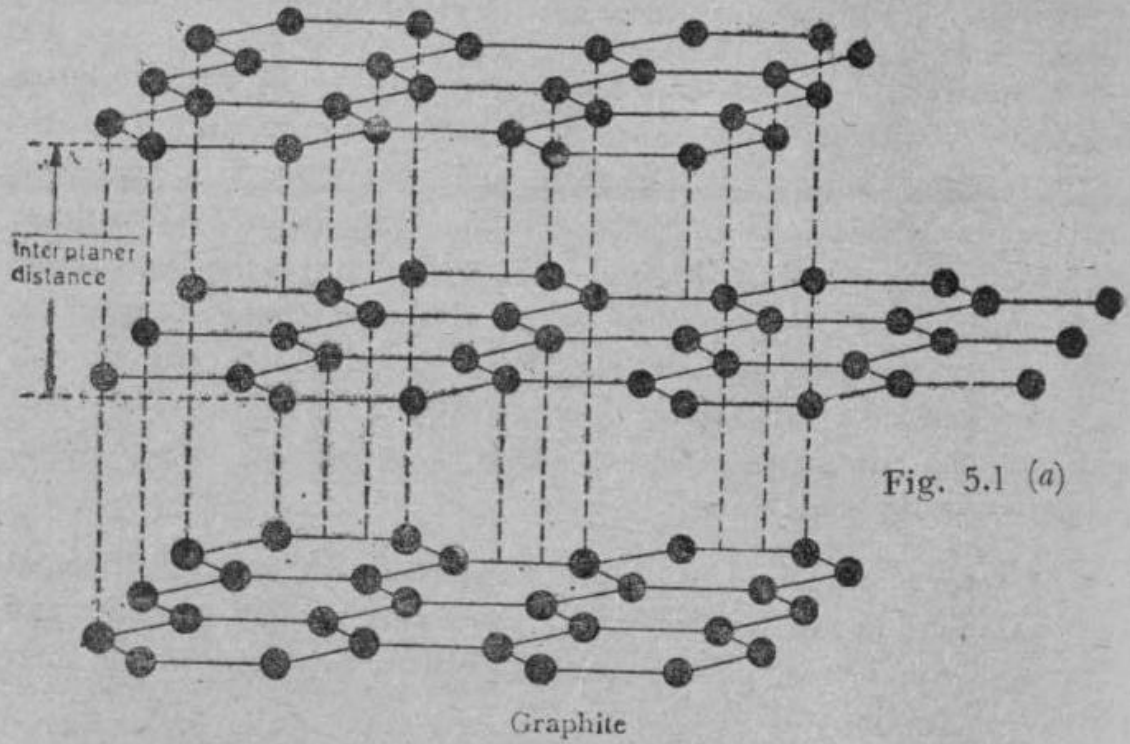
However, their combustion with oxygen indicates that the products (CO_2) thus obtained are exactly the same. Other chemical reactions of graphite and diamond reveal that they are, in fact, the same element. To explain the difference in properties given in the table above, chemists believe that the atoms of carbon in graphite and diamond must be arranged in different patterns. *Two or more forms of the same element which differ in the arrangement of atoms in the crystal lattice are known as allotropic forms.*

Energetically graphite is slightly more stable than diamond. The enthalpy change (ΔH) for the reaction.



is -0.453 kcal/mole .

The crystalline structures of graphite and diamond are given in Fig. 5.1 (a) and (b).



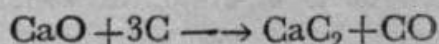
It should be noted that in diamond each carbon atom is covalently bonded to four other carbon atoms to give a tetrahedral arrangement. The C—C bond length in diamond is $1.54\text{-}\text{\AA}$ and bond energy is 85 kcal/mole which compares well with the organic molecules like ethane $\text{CH}_3\text{—CH}_3$.

In graphite carbon atoms form planar layers where each carbon atom is bonded with three other carbon atoms. The distance between each layer is of the order of $3.40\text{-}\text{\AA}$. The C—C bond distance in graphite is $1.415\text{-}\text{\AA}$ which suggests that the bonds are intermediate between single and double. The large distance between two layers ($3.40\text{-}\text{\AA}$) suggests that carbon atoms of one layer interact rather weakly with the carbon atoms of the other layer and hence forces of attraction between two layers would be extremely weak (Van der Waal forces). This point of view is confirmed by the observation that graphite has a slippery touch and hence is used as a lubricant. It conducts electricity (due to weakly bonded electrons) in the direction parallel to the layers of carbon atoms. The conduction of electricity in the direction perpendicular to the planes of carbon atoms is rather small. On the other hand, diamond due to covalently bonded carbon atoms is extremely rigid and a poor conductor of electricity.

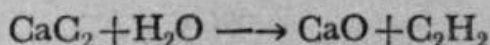
CHEMICAL PROPERTIES OF CARBON

Carbon is not very reactive at room temperature. At high temperatures carbon is more reactive and forms many compounds with different elements.

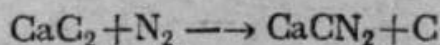
Carbides : Carbon can combine with metals and non-metals to form carbides. These compounds are formed by heating carbon with the other element or its compounds. Thus, calcium carbide is formed by heating calcium oxide with carbon at 3000°C in an electric furnace.



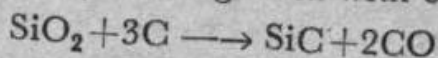
Calcium carbide reacts with water to give acetylene.



Calcium carbide is used for making acetylene and for making calcium cyanamide CaCN_2 .



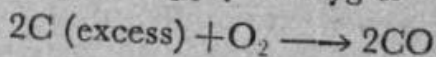
Silicon carbide is formed by heating silica with carbon



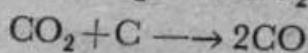
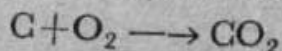
Silicon carbide has a diamond-like structure in which half of carbon atoms have been replaced by silicon. On the basis of this structure it is possible to predict that SiC should be hard. Because of this hardness SiC is used as an abrasive.

Oxides of Carbon : Carbon forms two oxides with oxygen : carbon monoxide and carbon dioxide.

Carbon monoxide : Carbon monoxide is formed when an excess of carbon is burnt in a limited supply of oxygen



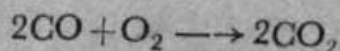
This reaction probably occurs in two steps. In the first step CO_2 is formed which then changes to CO by reaction with carbon.



When steam is passed over heated coal, a mixture of CO and H_2 , known as water gas, is produced.



Chemical Properties : Carbon monoxide burns in oxygen with a blue flame forming CO_2 .

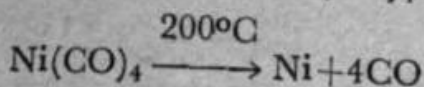
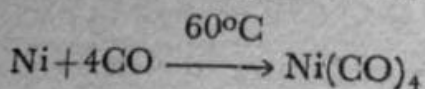


At high temperatures it reacts with metal oxides to form metal and CO_2 .

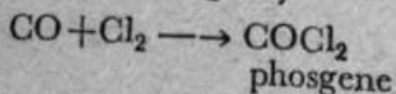


Synthetic petroleum is formed when a mixture of carbon monoxide and hydrogen (water gas) is passed over a catalyst at high temperature.

Carbon monoxide reacts with nickel to form nickel carbonyl $\text{Ni}(\text{CO})_4$. The reaction occurs when CO is passed over nickel metal at 60°C . $\text{Ni}(\text{CO})_4$ decomposes at 200°C forming nickel metal.



With chlorine CO forms COCl_2 (phosgene).

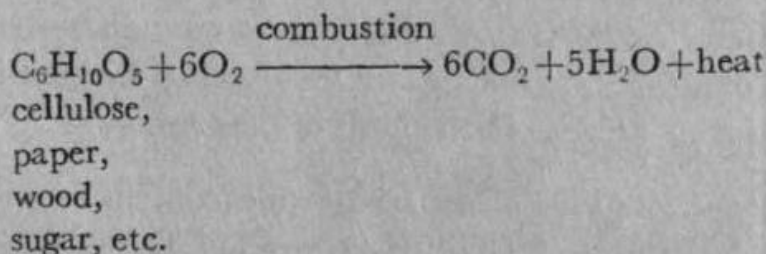
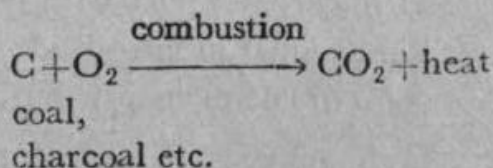


Phosgene is a poisonous gas and was used in the First World War.

Carbon monoxide is a very dangerous poison, especially because it is odourless and tasteless. Therefore it gives no warning of its presence. It interferes with the normal oxygen carrying function of the haemoglobin in the red blood cells. Instead of forming a complex compound with oxygen molecules, haemoglobin forms a more stable complex compound with CO (carboxy-haemoglobin). The tissue cells are thus starved of oxygen and death may result. Concentrations of 0.2 percent in air cause unconsciousness in about half an hour and death in about three hours.

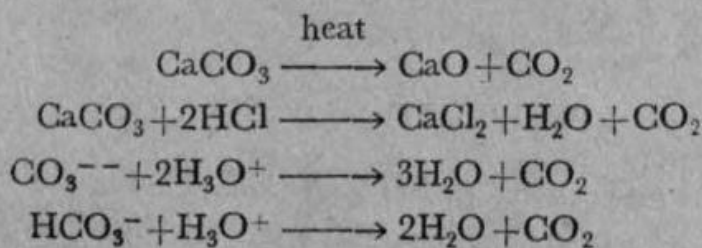
In big cities the large number of automobiles produce so much carbon monoxide that it is a health hazard. To lessen the hazard scientists are experimenting with various devices. One such method is to build a cell on top of the cylinder of a motor engine. The hot gases from the cylinder are led into this cell where air is injected which oxidizes carbon monoxide to carbon dioxide.

Carbon Dioxide : When organic matter burns or gets fermented carbon dioxide is formed.



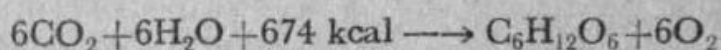
Commercially carbon dioxide is produced from carbonate minerals, from water gas or by fermentation of molasses.

Carbonates and bicarbonates when heated or when treated with an acid will produce carbon dioxide.



Properties of Carbon Dioxide : It is a colourless gas and is a non-supporter of combustion.

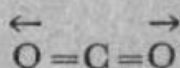
Carbon dioxide is formed during respiration and so is always present in the atmosphere. Its concentration in atmosphere however, does not keep increasing. This is because it is taken up by plants. In sunlight the green colouring matter of plants, chlorophyll, catalyses reaction between carbon dioxide and water to form carbohydrates which are then utilized by plants for making further complex compounds. It is a complicated reaction comprising of many steps, but the overall reaction is :



Such synthesis by plants in the presence of light is called photosynthesis.

Carbon dioxide is a gas at ordinary temperature and pressure but it can be obtained as a liquid and a solid. Solid carbondioxide is known as dry ice.

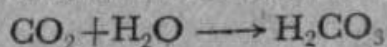
Carbon dioxide has a structure as shown below :



As the molecule is linear, the polarities of $\text{C}=\text{O}$ are oriented in opposite directions. Being equal in magnitude these cancel each other giving the molecule a zero dipole moment.

Carbon dioxide is soluble in water to the extent of 900 ml in one litre of water at 20°C . Aerated waters contain carbon dioxide at a pressure of 3—4 atmospheres. On opening the bottle the dissolved carbon dioxide escapes in the form of bubbles.

Aqueous solutions of carbon dioxide contain carbonic acid.



It has been found that 99% of the dissolved gas exists as free CO_2 , the remaining gas exists as H_2CO_3 .

Carbonic acid forms two series of salts, bicarbonates, and carbonates. The chemistry of the carbonates and bicarbonates of various metals has been discussed elsewhere.

PROPERTIES OF SILICON

The electronic configuration and the structure of silicon have already been described. Silicon has high melting point. The reason for this is the same as for carbon. Very high energy is needed to break the $\text{Si}-\text{Si}$ bonds. Silicon like carbon (diamond) is very hard.

The most important compound of silicon is SiO_2 . In the molecule of silicon dioxide there is a single bond between $\text{O}-\text{Si}$ (contrary to CO_2 , where there is a double bond $\text{C}=\text{O}$), thus in this way oxygen is attached by its two bonds to two atoms of Si, which in turn is further linked.

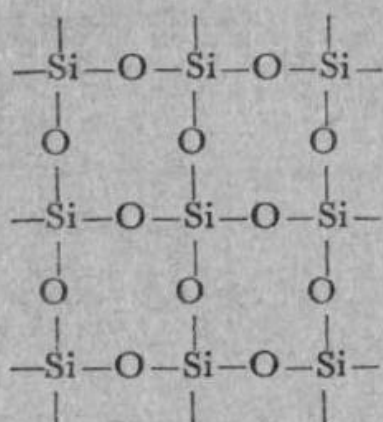
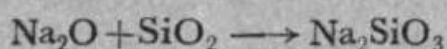
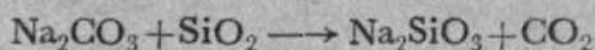


Fig. 5.2

By the repeated bonding of oxygen and silicon atoms a rigid network is formed, and from this net work it is not easy for any molecule to move out and get separated. When molecules cannot shift from one position to another, the phase is called a solid phase. So due to strong linkages of molecules SiO_2 exists as a solid at ordinary temperature.

Like carbon, silicon is not very reactive at ordinary temperature. At high temperatures it reacts with a number of elements.



Sodium silicate is marketed as a viscous white fluid and is used as a filler for soaps. It is soluble in water.

Insoluble Silicates : All naturally occurring silicates are insoluble. Familiar examples of silicates are sand, soil, kaolin, mica, etc.

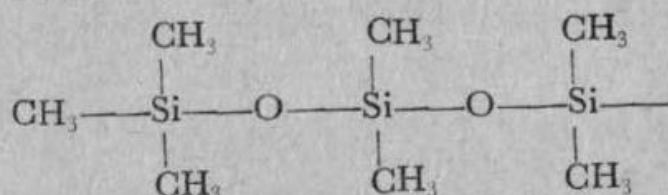
Silicates can be prepared artificially and familiar examples are cement, glass, ultramarine, porcelain, and earthenware vases. Cement is made by heating clay and lime to sintering temperature in a rotary kiln.

Glass is manufactured by fusing silica and sodium or calcium oxides with a variety of other oxides.

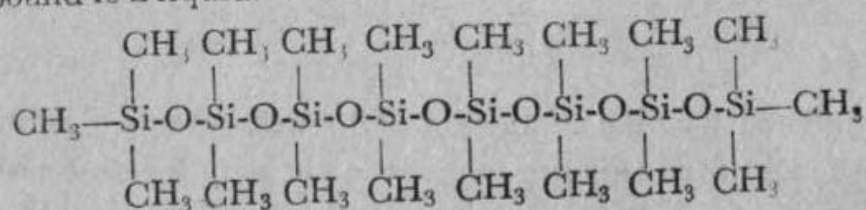
Ultramarine, the blue pigment used for laundering, is made by heating kaolin, sodium carbonate and sulphur together.

Hydrides of Silicon : Silicon forms hydrides like SiH_4 silane and Si_2H_6 di-silane. Such compounds are comparable to carbon hydrides, CH_4 and C_2H_6 .

Silicones : Silicones are an interesting class of compounds. Structure of one member, methyl silicone, is given below :



Properties of silicones have been found to depend on the length of the $\text{Si}-\text{O}-\text{Si}$ chains. When the chain is of eight atoms (see below), the compound is a liquid.

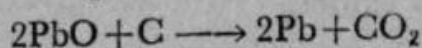
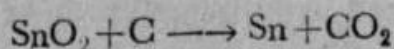


With longer chains, more viscous liquids or grease and jelly-like compounds or rubber-like materials are obtained. Liquid silicones are used as lubricants. One desirable property of lubricants is that they should have uniform viscosity over a wide range of temperature, so that when a machine becomes hot during running, the lubricants should not become thin and flow out. Again lubricants should be very stable under adverse conditions of temperatures. Silicones possess both these properties. They are very stable at high temperature and as for their viscosity it has been found that their viscosity may change by about 7 units for a change in temperature from 30° to 100°F . While for ordinary organic lubricants the viscosity might change by 1800 units.

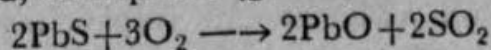
Silicones are also used as water repellants. These are used for water-proofing paper, cloth, glass and porcelain.

TIN AND LEAD

Tin and lead, both are prepared from their oxides by reduction with carbon.



In the case of lead, its sulphide (galena) is first converted into PbO .



Tin is a white metal and occurs in two allotropic forms, the ordinary tin and the grey tin. Grey tin has a structure like diamond.

Tin reacts with hydrochloric acid to form stannous chloride. When tin reacts with chlorine, SnCl_4 is formed.

Tin is used for tin plating. Vegetable ghee tins, for example, are made of iron sheets coated with tin plating. Tin plating is done by dipping iron sheets in molten tin.

Tin plating prevents iron from rusting. When coating of tin is broken then the corrosion of iron will be more rapid than if the iron was uncoated. A look at oxidation potentials will show that Fe is more reactive than tin and a galvanic cell is set up between iron and tin, whereby Fe gets corroded rapidly.

Lead mostly forms divalent compounds. This can be explained by considering Table 5.1. If the two s electrons in the outermost shell would not unpair then the valency of lead will be only two.

Compounds: Lead chloride is white. It is insoluble in cold water but dissolves in hot water. Lead sulphide is black in colour and is insoluble in dilute acids.

Stannous sulphide is brown black and stannic sulphide is yellow. Sulphides of tin are insoluble in dilute acid but dissolve in yellow ammonium sulphide. Lead sulphide is insoluble in yellow ammonium sulphide.

Questions

1. Draw diagrams showing the arrangement of atoms in (a) diamond and (b) graphite. Which one is energetically more stable?
 2. Give possible explanations for :
 (a) CO_2 is a gas, SiO_2 is a solid; and
 (b) melting point of carbon is more than 4000°K , while that of tin is 505°K .
 3. Tin and lead are both metals. Write down two reactions in which their chemical behaviour is similar. Give one reaction to show that tin differs from lead.
 4. What is allotropy? Give different allotropic forms of carbon and tin.
 5. How are carbon monoxide and carbon dioxide prepared in the laboratory? Why is carbon monoxide so poisonous?
-

CHAPTER 6

Group V

THE NITROGEN FAMILY

Group V consists of nitrogen (N), phosphorus (P), arsenic (As), antimony (Sb), and bismuth (Bi). The elements and compounds in this group show a wide variation in physical and chemical properties.

GENERAL CHARACTERISTICS

Some of the physical properties are given in Table 6.1. As shown, each element has the s^2p^3 configuration and thus has three electrons less than the number of electrons required to fill the outer-most energy levels. The five outer electrons in each case consist of two s orbital electrons and three p orbital electrons.

Oxidation states of -3 , $+3$ and $+5$ are common for all the elements. The nitrogen family elements exhibit the -3 oxidation state in their hydrides. They show a maximum oxidation state $+5$ by using all the five electrons in the outermost orbit in forming bonds. The tendency of the unshared pair of s electrons to remain inert (the *inert pair effect*), increases with the increase in atomic weight. Thus, only the p electrons are used in bonding, showing $+3$ oxidation state of the element. In the case of nitrogen, oxidation states of -2 , $+1$, $+2$ and $+4$ are also important.

antimony There is an increase in electropositive (metallic) character down the group. Nitrogen and phosphorus are non-metals, arsenic and antimony are metalloids, and bismuth is a true metal. Thus, the oxides of nitrogen and phosphorus are strongly acidic, whereas those of arsenic and (stibium) are amphoteric and those of bismuth largely basic. The increasing basicity of oxides going down the group is mainly attributed to the increasing size of the elements.

The ionization potentials indicate that it is much more difficult to remove electrons from a nitrogen atom than from a bismuth atom. Since nitrogen atom is a small one, it holds its electrons firmly and forms multiple bonds. Under ordinary conditions, other members of the

group are not able to form diatomic molecules. Instead, at least in some of their allotropic forms, phosphorus, arsenic and perhaps antimony occur as separate tetraatomic, tetrahedral molecules. The tendency to form covalent linkages is reduced as the group is descended.

Ionic structures are less common in this group than in the compounds of groups I, II, VI and VII, as would be expected from the intermediate electronegativity values. Again, a wide range of behaviour in group V is shown by anion formation by nitrogen and cation formation by bismuth, *e.g.* Li_3N and BiF_3 . It may be noted that nitrogen is the only member of the group which can accept three electrons to complete its octet, thus forming N^{3-} , the nitride ion. Moreover, the loss of all the five outer electrons is not encountered because no M^{5+} cations are formed.

Nitrogen resembles its neighbours, carbon and oxygen in the formation of multiple bonds. It combines with itself to form a triply bonded diatomic molecule, $:\text{N}:::\text{N}:$, which has a very short internuclear distance ($1.09\text{-}\text{\AA}$) and a very high bond strength. Thus, chemically nitrogen is very inert as a large amount of energy is required to disrupt the molecule (dissociation energy = 225 kcal/mole).

Nitrogen differs widely from other members of the group. The differences can be attributed to (1) a small size, (2) inability to accommodate more than eight electrons in the valence shell, (3) great electronegativity, and (4) great stability of the free element. Nitrogen cannot form complexes by accepting electron pairs, as its valence shell is limited to an octet. The other members can form such complexes owing to the availability of suitable vacant *d* orbitals, and can show the maximum co-ordination number 6.

Table 6.1
SOME PHYSICAL PROPERTIES OF GROUP V ELEMENTS

Symbol	At. No.	Electronic configuration	Atomic radius ($\text{\AA}^\circ$)	m.p. $^\circ\text{C}$	b.p. $^\circ\text{C}$	First ioniza- tion potential (e. v.)	Electro- negativity
N	7	(He) $2s^2 2p^3$	0.74	-210.0	-195.8	14.5	3.1
P	15	(Ne) $3s^2 3p^3$	1.10	44.1	280	11.0	2.1
As	33	(Ar) $3d^{10} 4s^2 4p^3$	1.21	814.0 (36 atm)	633 (sublimes)	10.0	2.0
Sb	51	(Kr) $4d^{10} 5s^2 5p^3$	1.41	630.5	1325	8.6	1.8
Bi	83	(Xe) $4f^{14} 5d^{10} 6s^2 6p^3$	1.52	271.0	1560	8.0	1.7

ELEMENTS

OCCURRENCE

Nitrogen is the only member of group V that occurs as a gas in the elemental state. It comprises about 78% of the earth's atmosphere. In combined form it occurs mainly as sodium nitrate (Chile Salt peter). Plants and animals contain combined nitrogen in the form of proteins.

Phosphorus is the only member of the family which is never found in the free state in nature because of its considerable reactivity. It occurs mostly in the form of phosphates—the simple calcium phosphate $\text{Ca}_3(\text{PO}_4)_2$, and the mixed phosphate $\text{CaF}_2 \cdot 3\text{Ca}_3(\text{PO}_4)_2$, known as *apatite*. Ores containing large percentages of calcium phosphate are commonly known as *phosphate rocks*. Phosphorus is an essential element of all animal and vegetable matter. It is the principal mineral constituent of bones and teeth. The human body contains about 1 per cent of phosphorus.

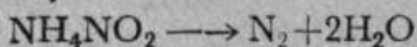
Arsenic occurs principally as sulphides—*orpiment* (As_2S_3), *realgar* (As_4S_4) and *arsenopyrite* (FeAsS). It is sometimes found in nature in the uncombined state.

Antimony occurs chiefly in the mineral *stibnite* (Sb_2S_3). Small quantities of the element may be found in the free state.

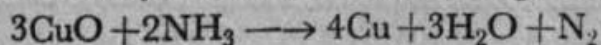
Bismuth is found in both the free and the combined state. The principal minerals of bismuth are *bismuth glance* (Bi_2S_3) and *bismuth ochre* (Bi_2O_3).

PREPARATION

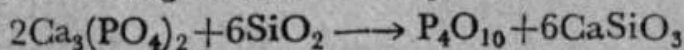
Nitrogen is obtained commercially by the fractional distillation of liquid air. Pure nitrogen can be prepared in the laboratory by heating ammonium nitrite carefully :



Another simple method for the preparation of nitrogen gas is the reduction of cupric oxide by ammonia at high temperatures :

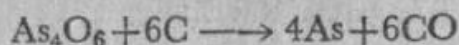


Phosphorus is prepared industrially by heating a mixture of phosphate rock, sand and coke to a high temperature in an electric furnace. The following reactions take place :

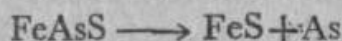


The phosphorus and the carbon monoxide escape as vapours and the former is condensed under water as a white waxy solid.

Arsenic is easily obtained by reducing arsenious oxide, As_2O_3 , with carbon :

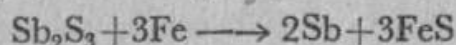


The element can also be obtained by heating the mineral arsenopyrite in the absence of air :

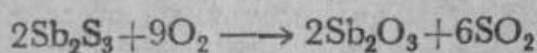


Antimony is prepared from the sulphide ore in two ways :

(i) By heating it with scrap iron :



(ii) Converting the sulphide ore to oxide by roasting, which is then reduced with carbon in the form of charcoal or coke :



Purification of the metal may be achieved electrolytically.

Bismuth is produced mostly as a by-product in the extraction of lead and in the refining of copper. Like arsenic and antimony, it may be recovered from the sulphide ore by roasting, followed by reduction with carbon.

HYDRIDES

All the elements form simple hydrides of formula MH_3 . They are all colourless gases under ordinary conditions. The ease of formation, stability, ability to use the lone pair of electrons for coordinate bond formation and the ease of replacing the hydrogens by elements of other groups decreases from NH_3 to BiH_3 .

Some of the physical properties are listed in Table 6.2.

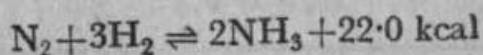
Table 6.2

SOME PHYSICAL PROPERTIES OF GROUP V HYDRIDES

Hydride	M.P.(°C)	B.P. (°C)	Odour
Ammonia	- 78	-33	pungent
Phosphine*	-134	-87	decaying fish
Arsine*	-114	-55	garlic-like
Stibine*	- 91	-18	disagreeable
Bismuthine	..	+22	...

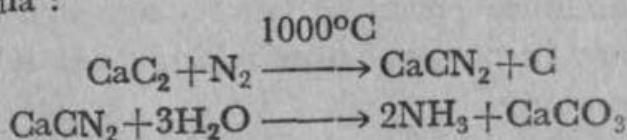
*Exceptionally poisonous.

The most important industrial method for producing ammonia is the *Haber process*, in which nitrogen combines directly with hydrogen according to the equation :



Le Chatelier's principle suggests high pressure and low temperature for favourable formation of ammonia. In actual practice, the process is carried out at a temperature of about 500°C and at a pressure of 200 atmospheres in the presence of a catalyst mixture, such as Fe_3O_4 and $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3$.

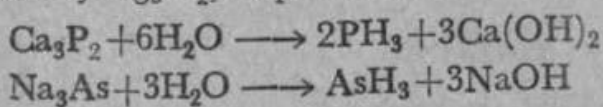
Ammonia is also produced on a large scale by the *Cyanamide process* which is based on the reaction of nitrogen gas with calcium carbide, CaC_2 , in an electric arc furnace at about 1000°C . The resulting calcium cyanamide CaCN_2 , which is also used as a fertilizer, is treated with steam to form ammonia :



Commercially, ammonia may be obtained as a by-product in the production of coke, which involves the destructive distillation of bituminous (soft) coal. The ammonia is removed from the other gases by absorption in water.

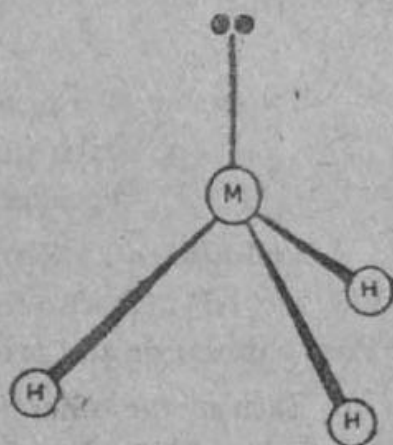
Most of the ammonia is used in the manufacture of nitric acid and fertilizers, *e.g.* ammonium sulphate.

Phosphine, arsine, stibine and bismuthine may be prepared by the action of water or dilute acid on calcium phosphide, Ca_3P_2 , sodium arsenide Na_3As , calcium antimonide or stibide Ca_3Sb_2 and magnesium bismuthide, Mg_3Bi_2 , respectively :



The structure of these hydrides is pyramidal, or tetrahedral with one position occupied by a lone pair as shown below :

There is a steady increase in boiling point and melting point from PH_3 through the other members which indicates stronger interactions between hydride molecules. The relatively high melting point and boiling point of ammonia are the result of its ability to develop hydrogen bonding.



Tetrahedral structure of 5th group hydrides

Fig. 6.1

The stability of these hydrides decreases on descending the group as indicated by their bond energies listed in Table 6.3.

Table 6.3

Bond	Bond Energy (kcal/mole)
N—H ..	93
P—H ..	76
As—H ..	59
Sb—H ..	61

Ammonia is the most stable of these gases. Phosphine and arsine are fairly stable, but stibine breaks up into antimony and hydrogen quite readily. Bismuthine breaks up into its constituent elements very readily. It can only be prepared in trace amounts, and it decomposes at quite low temperatures.

Only nitrogen and phosphorus form tetrahedral MH_4^+ cations. Ammonia forms ammonium NH_4^+ salts very readily, and utilizes the lone pair of electrons to form a co-ordinate bond. Phosphine reacts with gaseous hydrogen chloride, bromide and iodide to form phosphonium PH_4^+ salts. As phosphine is a much weaker base than ammonia, its salts are much less stable. The most commonly known phosphonium salt is the iodide, PH_4I . It exists in the solid state and is strongly hydrolysed by water (contrast ammonium halides).



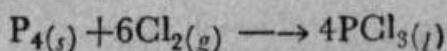
HALIDES

Two series of simple halides are known :

- (a) Trihalides, MX_3 , and
- (b) Pentahalides, MX_5 .

Trihalides : Nitrogen forms a very stable, unreactive gaseous fluoride, NF_3 . It also forms an unstable explosive liquid chloride, NCl_3 . Pure tribromide and tri-iodide compounds are unknown.

Each of the other four elements form each of the four possible trihalides. They can be prepared by direct reaction of the elements in stoichiometric proportion, *e.g.*



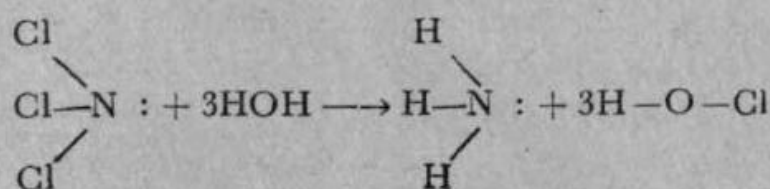
The reactions are all exothermic.

These trihalides are predominantly covalent and, like NH_3 , have a tetrahedral structure with one position occupied by a lone pair. BiF_3 is, however, ionic in character. Increasing electropositivity of the elements towards the bottom of the group imparts ionic character to the bonding, and this is reflected by the increase in the melting and boiling points, as indicated in Table 6.4.

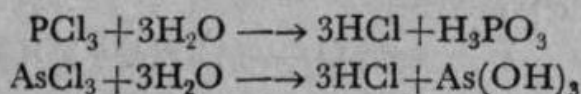
Table 6.4
SOME PHYSICAL PROPERTIES OF GROUP V
HALIDES

Trichlorides	M.P. ($^{\circ}\text{C}$)	B.P. ($^{\circ}\text{C}$)	Appearance
NCl_3 ..	—	71	yellow explosive oil
PCl_3 ..	-92	76	colourless volatile liquid
AsCl_3 ..	-16	130	colourless liquid
SbCl_3 ..	73	221	soft, colourless mass
BiCl_3 ..	232	441	white solid

Nitrogen trichloride is hydrolysed to form ammonia and hypochlorous acid. Co-ordination to a hydrogen atom of a water molecule occurs through the lone pair of electrons of the nitrogen atom, as shown below :

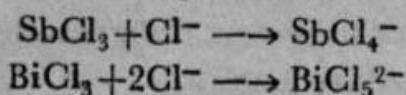


Since phosphorus, arsenic and antimony can expand their octet their trihalides hydrolyse readily, giving the appropriate oxy-acids:



The extent of hydrolysis diminishes as the metallic character of the group V element increases.

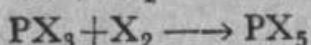
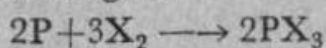
With the exception of NCl_3 the trihalides have a tendency to act as electron 'acceptors' and can undergo addition reactions *e.g.*



PCl_3 reacts readily with oxygen to form the oxychloride, POCl_3 . The molecule is tetrahedral. The oxidation state of phosphorus in this molecule is +5.

Pentahalides : There are no pentahalides of nitrogen, this being consistent with the fact that the nitrogen atom is unable to expand its octet owing to the absence of d orbitals. All the pentahalides of phosphorus, excepting the iodide, are known. It is apparently impossible for five large iodine atoms to fit around the relatively small phosphorus atom. Only four pentahalides of arsenic, antimony and bismuth are known. They are AsF_5 , SbF_5 , BiF_5 , and SbCl_5 .

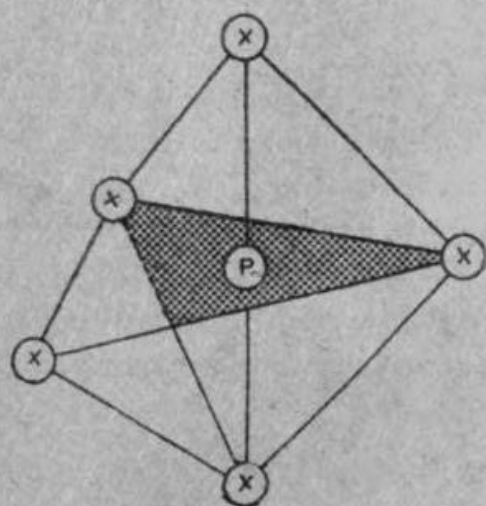
The pentahalides are prepared either by direct reaction of excess halogen with the element, or by further reaction of the trihalide with the appropriate halogen :



(X = F, Cl, Br)

The pentahalide molecules have the trigonal bipyramid structure in the gas phase as shown below :

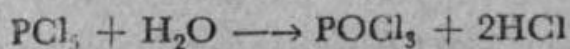
A trigonal bipyramid is not a regular structure and is, thus, not very stable. In the solid state, PCl_5 exists as $[\text{PCl}_4]^+$ cations and $[\text{PCl}_6]^-$ anions which have tetrahedral and octahedral structures respectively.



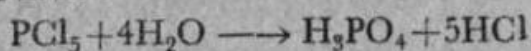
Trigonal bipyramidal structure of pentahalides

Fig. 6.2

Hydrolysis of PCl_5 give rise to the oxychloride POCl_3 ,



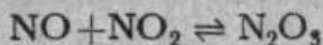
but in excess water the following reaction producing orthophosphoric acid, H_3PO_4 , is dominant :



OXIDES

The most important oxides of the group are trioxides and pentoxides having the empirical formulas M_2O_3 and M_2O_5 respectively. Here, the elements of group V show oxidation numbers of +2 and +5 respectively. Because of somewhat different chemistry of nitrogen, its other oxides are discussed separately.

Trioxides : Dinitrogen trioxide or nitrogen sesquioxide is a covalent compound having the formula N_2O_3 . It is unstable and is obtained pure only in solid form (pale blue, m.p. = -102°C). It is prepared as a blue liquid with a boiling point 3.5°C by the union of equimolar quantities of nitric oxide and nitrogen dioxide at -20°C .



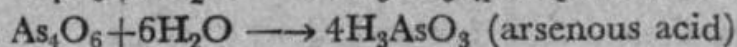
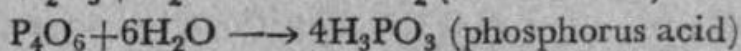
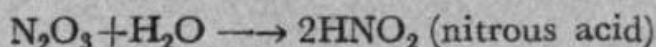
Phosphorus sesquioxide is obtained by oxidising white phosphorus at about 100°C in a limited supply of air. It is a white crystalline solid which melts at 23.8°C and boils at 175.4°C . The molecular weight measurements show that it exists in the form of P_4O_6 molecules. It is interesting to note that the tetrahedral structure formed in the P_4 molecule is maintained for phosphorus in P_4O_6 . Phosphorus trioxide is thus dimeric and should be written as P_4O_6 and not P_2O_3 .

When burnt in air, arsenic antimony and bismuth are oxidized to sesquioxides. The sesquioxides of arsenic and antimony are assigned the formulas As_4O_6 and Sb_4O_6 . Bismuth sesquioxide is not dimeric and is assigned the empirical formula Bi_2O_3 . These sesquioxides are solids at ordinary temperatures, As_4O_6 and Sb_4O_6 being white and Bi_2O_3 yellow.

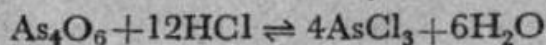
These sesquioxides show a clear trend from acidic to basic character down the group :

N_2O_3	P_4O_6	As_4O_6	Sb_4O_6	Bi_2O_3
acidic	acidic	amphoteric	amphoteric	basic

Thus N_2O_3 , P_4O_6 and As_4O_6 each react with water to form acids :



Whereas nitrogen and phosphorus sesquioxides have no basic properties, arsenious sesquioxide dissolves more readily in HCl than it does in water :

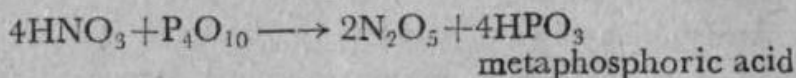


Antimony and bismuth sesquioxides are insoluble in water. Antimony sesquioxide is amphoteric, with basic character being much more pronounced than in the corresponding arsenic compound. Sb_2O_3 reacts with OH^- and H^+ ions to yield antimonite and antimonyl ions respectively :

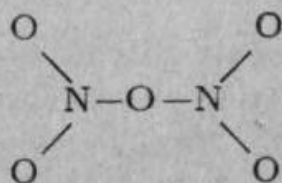


Bismuth trioxide is completely basic in character and is soluble in acids but insoluble in solutions of bases. The even greater metallic character of the Bi_2O_3 is entirely consistent with the fact that of all the elements in the group bismuth has the largest atomic radius and lowest electronegativity.

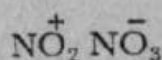
Pentoxides : Dinitrogen pentoxide is a white, volatile solid, subliming at 32°C . This compound, with the empirical formula N_2O_5 , is the anhydride of HNO_3 . It is prepared by dehydrating HNO_3 with P_4O_{10} :



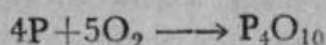
In the gas phase, nitrogen pentoxide consists of simple N_2O_5 molecules and has the structure :



In the solid state, it exists as nitronium nitrate,



Phosphorus pentoxide is a misleading term as vapour density measurements show the true molecular formula to be P_4O_{10} . It is a white deliquescent solid, subliming at 358°C . It may be prepared by burning phosphorus in an excess of air or oxygen :



Phosphorus pentoxide is the anhydride of phosphoric acid.

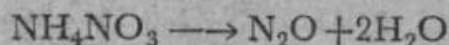
The most important chemical characteristic of phosphoric anhydride is its tremendous affinity for water. This property makes the oxide one of the most useful drying agents. With water phosphorus pentoxide gives first metaphosphoric acid, HPO_3 , which hydrates further to pyrophosphoric acid, $\text{H}_4\text{P}_2\text{O}_7$, and finally to orthophosphoric acid, H_3PO_4 .

All of the pentoxides of Group V elements are acidic in character. Whereas N_2O_5 and P_4O_{10} react readily with water to yield nitric acid and phosphoric acids, arsenic pentoxide dissolves slowly in water to give a solution of arsenic acid, H_3AsO_4 . Antimony pentoxide is only sparingly soluble in water, but gives an acidic solution. No free antimononic acid derived from the oxide has been prepared, but antimonates

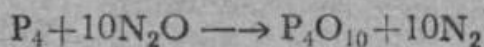
containing $\text{Sb}(\text{OH})_6$ are known. Bismuth pentoxide is insoluble. It does have acidic properties and alkaline bismuthates are known, *e.g.*, sodium bismuthate, NaBiO_3 .

These oxides illustrate an important generalization that can be applied to all the groups of the Periodic Table, *i.e.*, the stability of the highest oxidation states decreases on descending the group. The usual trend that higher oxidation states are more-acidic is also observed.

Nitrous Oxide, N_2O : It is prepared by heating gently ammonium nitrate.

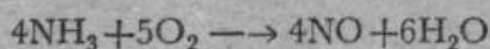


The gas is colourless with a faint sweetish smell, and is fairly soluble in water at low temperatures. Chemically it is unreactive at ordinary temperature. The solution of nitrous oxide in water is neutral. Materials that burn in air do so even more brightly in N_2O , because (i) the gas readily gives up its oxygen, forming N_2 , and (ii) it contains 33% oxygen by volume as against the 20% in air, *e.g.*

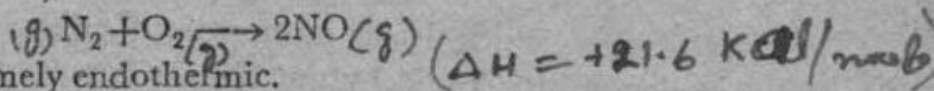


When inhaled in low concentrations, N_2O produces a mild hysteria (hence its common name "laughing-gas"). It is used as an anaesthetic.

Nitric Oxide, NO . It can be produced in a variety of ways. The gas is of commercial importance in the manufacture of nitric acid. The most important industrial method is the catalytic oxidation of ammonia:

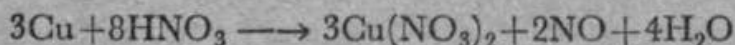


Nitric oxide can also be made by sparking nitrogen and oxygen (Birkeland-Eyde Process) :



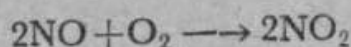
This reaction is extremely endothermic.

Nitric oxide is a reduction product of nitric acid and is conveniently prepared in the laboratory by the action of dilute nitric acid on copper metal :

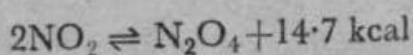


The gas is colourless and relatively insoluble in water, and is the most stable of the oxides of nitrogen. The nitric oxide is one of the few "odd" molecules known, containing an odd number of electrons. This means that one electron must be unpaired. The odd electron is not located solely on either the nitrogen atom or the oxygen atom, but rather belongs to the molecule as a whole. Such an electron is said to be *delocalized*.

Nitric oxide is fairly reactive, but not as highly reactive as would be expected of an odd molecule. It combines readily with atmospheric oxygen to give brown NO_2 :

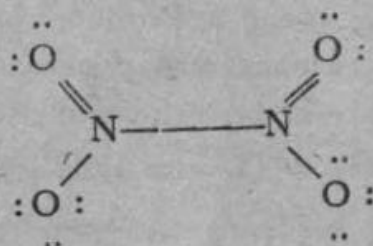


Nitrogen Dioxide and Dinitrogen Tetroxide : Nitrogen dioxide, NO_2 , a red-brown gas, and its dimer, dinitrogen tetroxide, N_2O_4 , a colourless gas, exist in equilibrium with one another at ordinary room temperatures :

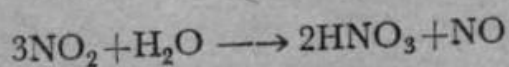


The above equation shows that the formation of N_2O_4 is favoured at low temperatures.

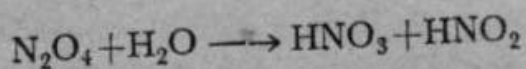
Nitrogen dioxide is an angular molecule with an $\text{O}-\text{N}-\text{O}$ angle of 132° . Like nitric oxide, the dioxide is an "odd" molecule and is paramagnetic. When nitrogen dioxide gas is cooled, the brown colour fades and the paramagnetism diminishes. It is suggested that two NO_2 molecules combine (dimerize) to form a single colourless molecule of N_2O_4 . The dimer has no unpaired electrons and the solid has the following structure :



1 Nitrogen dioxide is an intermediate compound formed in the preparation of nitric acid by the Haber-Ostwald Process. When NO_2 is dissolved in water, oxidation and reduction take place within the molecules of NO_2 (*auto-oxidation*) to yield nitric acid and nitric oxide.



Both NO_2 and N_2O_4 are strong oxidizing agents and with water they give a mixture of nitric and nitrous acids :



The strong oxidizing power of NO_2 finds application in the lead chamber process for the production of sulphuric acid where it is used to oxidize sulphur dioxide to sulphur trioxide at normal temperatures.

OXYACIDS

The important trivalent and pentavalent oxyacids of Group V are given below in Table 6.5.

Table 6.5

OXYACIDS OF GROUP V ELEMENTS

Ox. State	N	P	As	Sb	Bi
+3	HNO ₂	H ₃ PO ₃	H ₃ AsO ₃	..	..
+5	HNO ₃	H ₃ PO ₄	H ₃ AsO ₄	HSb(OH) ₆	HBiO ₃

We have already mentioned that the oxides of nitrogen, phosphorus and arsenic are acidic in character, and when hydrolysed with water, they yield the corresponding hydroxy compounds. The oxides, their corresponding acids, their acidity constants (K_a) and the formulas of the oxyions are listed in Table 6.6.

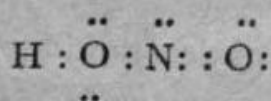
Table 6.6

ACIDITY CONSTANTS OF OXYACIDS

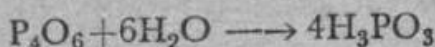
Oxide		Oxyacid	K _a	Oxyion
N ₂ O ₃	..	NO(OH)	4×10^{-4}	NO ₂ ⁻
N ₂ O ₅	..	NO ₂ (OH)	1×10^{-1}	NO ₃ ⁻
P ₄ O ₆	..	HPO(OH) ₂	1×10^{-2}	H ₂ PO ₃ ⁻
P ₄ O ₁₀	..	PO(OH) ₃	8×10^{-3}	H ₂ PO ₄ ⁻
As ₄ O ₆	..	As(OH) ₃	6×10^{-10}	H ₂ AsO ₃ ⁻
As ₄ O ₁₀	..	AsO(OH) ₃	5×10^{-3}	H ₂ AsO ₄ ⁻

TRIVALENT OXYACIDS

Nitrous Acid, HNO₂ : Pure nitrous acid is so unstable that it cannot be isolated, but is known only in solution. It is a weak acid, its equilibrium constant, K, being 4.0×10^{-4} mole/liter. Nitrous acid is formed together with nitric acid when NO₂ is dissolved in water. The electronic structure of the acid molecule is given below :



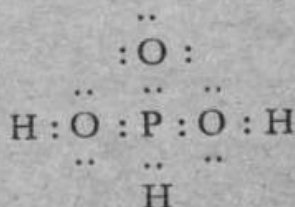
Phosphorous Acid, H_3PO_3 : Phosphorous acid is made by dissolving phosphorous trioxide in cold water :



It may also be prepared by the action of water on phosphorous trichloride :



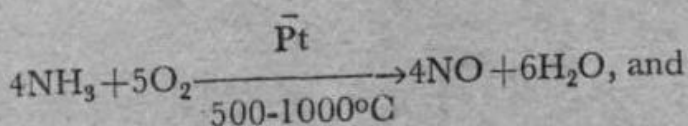
It is a colourless, deliquescent solid (m.p. 74°C) and is highly soluble in water. Phosphorous acid is a moderately strong acid, and has thus been assigned the electronic structure.



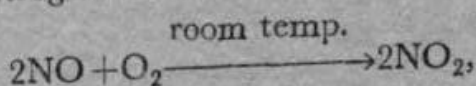
PENTAVALENT OXYACIDS

Nitric Acid, HNO_3 : Nitric acid is one of the most important industrial chemical and is produced commercially by the catalytic oxidation of ammonia (Ostwald process). The essential steps in the process are :

- (1) the oxidation of ammonia to nitric oxide



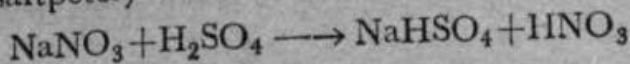
- (2) the union of nitric oxide with atmospheric oxygen to form nitrogen dioxide.



- (3) the reaction of nitrogen dioxide with water to produce nitric acid and nitric oxide.

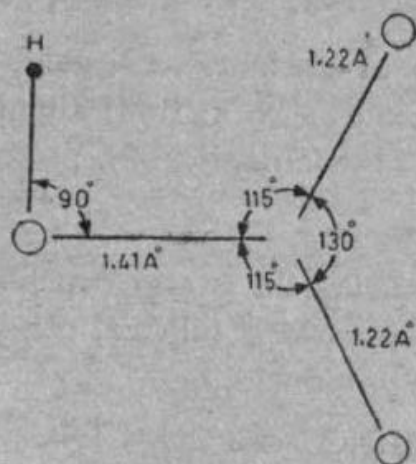
The NO produced is again mixed with air and converted to NO_2 . The acid, thus obtained, is about 60 per cent HNO_3 , and may be concentrated by distillation. The commonly known concentrated acid contains 68% HNO_3 , having specific gravity 1.4.

A considerable quantity of nitric acid is made by heating sodium nitrate (Chile saltpeter) with concentrated sulphuric acid :

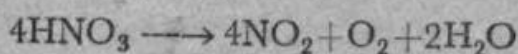


Pure nitric acid is a colourless liquid which freezes at -41.6°C and boils at 83°C . In the gas phase, the HNO_3 molecule has a triangular

arrangement. It has a planar structure in which various atoms are arranged as given below:



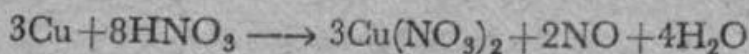
Chemically, nitric acid is characterized by its acid, oxidizing and nitrating properties. Pure acid has no action on metals or carbonates and behaves as a covalent liquid. On exposure to sunlight, it decomposes into nitrogen dioxide, oxygen and water.



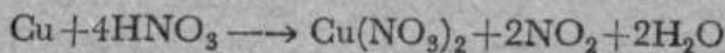
The acid is miscible with water in all proportions and acts as a strong acid in this medium. In dilute aqueous solutions, it completely dissociates into H^+ and NO_3^- .

Nearly all metals are attacked by nitric acid. The action is complex and the nature of the products depends on (i) the concentration of nitric acid, (ii) the nature of the reducing agent and (iii) the temperature. Most metals easily reduce nitric acid. Usually NO is the major product from dilute acid solutions and NO_2 is the major product from concentrated acid solution. A typical example is that of copper :

with *dil.* HNO_3

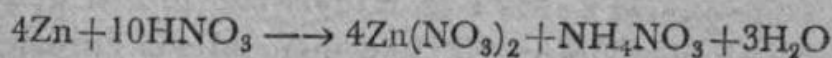


with *conc.* HNO_3

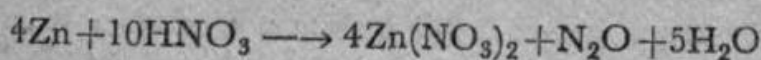


With strongly reducing metals like Zn and Sn , nitric acid tends to be reduced to the lower nitrogen oxidation states exhibited by N_2O and NH_4^+ , i.e.,

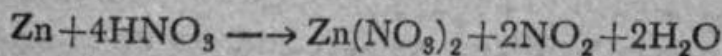
very dilute HNO_3



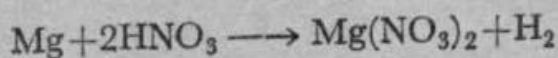
dil. HNO_3



conc. HNO_3

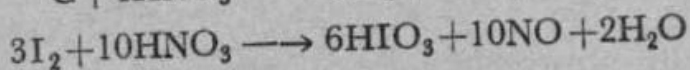
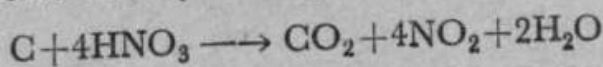


Magnesium and Manganese are the only metals that liberate H_2 :

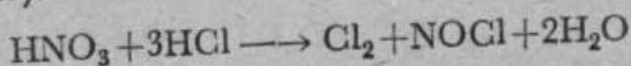


The noble metals, such as platinum and gold, resist the oxidizing action, while certain metals, such as iron, aluminium and chromium, become "passive" due to the formation of a protective coating of metal oxide.

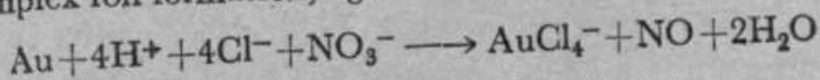
Hot concentrated nitric acid is also capable of oxidizing several of the non-metals such as carbon, sulphur, phosphorus and iodine to the corresponding oxide or oxyacid. *e.g.*,



A mixture of one part by volume of concentrated nitric acid and three parts by volume of concentrated hydrochloric acid is called *aqua regia* (royal water).

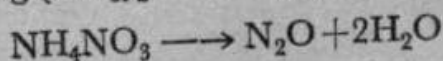
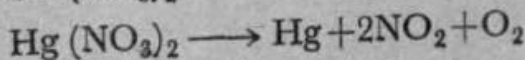
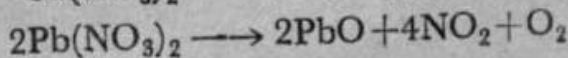
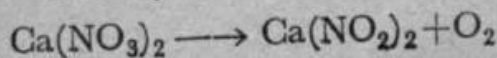
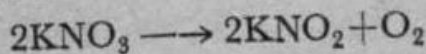


It dissolves such noble metals as gold and platinum which are inactive in either of the acids alone. The extra solvent power is the result of complex ion formation, *e.g.*



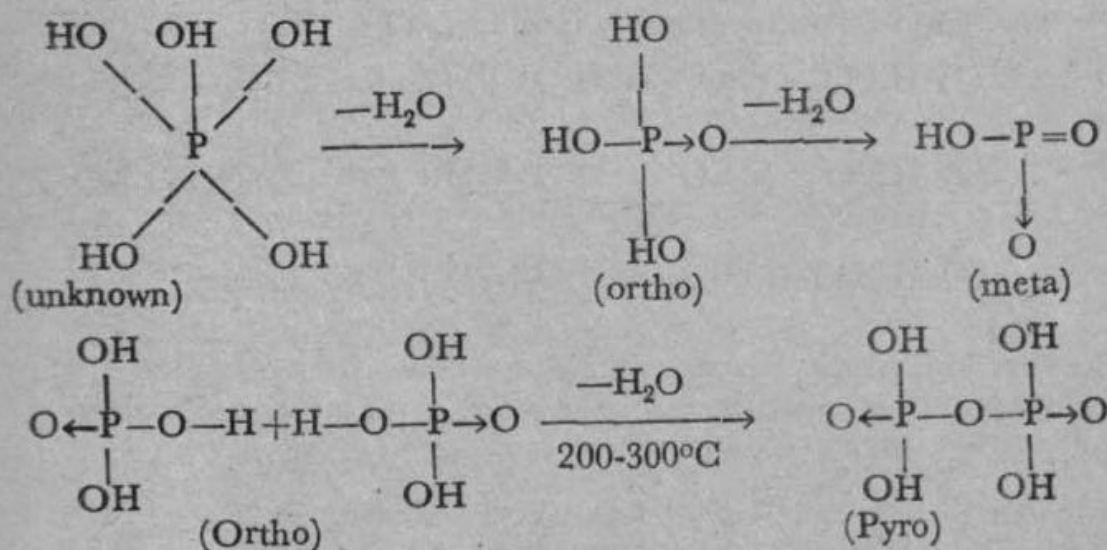
The nitrates are generally very soluble in water. Some of the exceptions are bismuth nitrate, $Bi(NO_3)_3$, and mercuric nitrate, $Hg(NO_3)_2$.

The nitrates are decomposed by heat. The products of decomposition depend on the nature of the positive ion, *e.g.*



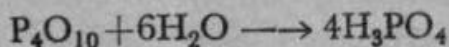
Phosphoric Acids : It is important to note that each phosphorus atom in *all* phosphoric acids and their salts is surrounded tetrahedrally by four oxygen atoms. No instance is known where phosphorus is directly attached to another phosphorus atom. Moreover, none of these acids is a good oxidizing agent (contrast with nitrogen).

Phosphorus pentoxide on hydrolysis, might be expected to produce the hydrated ortho acids H_5PO_5 , i.e. $\text{P}(\text{OH})_5$. Nevertheless no such compound or its derivatives have been isolated. Phosphorus pentoxide is the anhydride of three phosphoric acids which differ from one another only in the degree of hydration of oxide. The relationship between the different phosphoric acids is shown below :

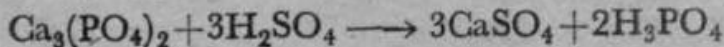


The most hydrated of the acid is the *ortho* acid, the least hydrated the *meta* acid ; the pyro acid represents an intermediate degree of hydration.

The most important phosphoric acid is the ortho compound. Orthophosphoric acid of high purity is prepared on an industrial scale by complete hydrolysis of P_4O_{10} :

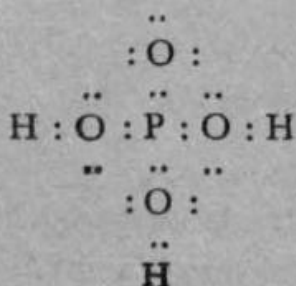


It is also obtained commercially by treating calcium phosphate in phosphate rock with 60% sulphuric acid.



The insoluble calcium sulphate is filtered off, and the solution is concentrated to about 85% phosphoric acid by evaporation.

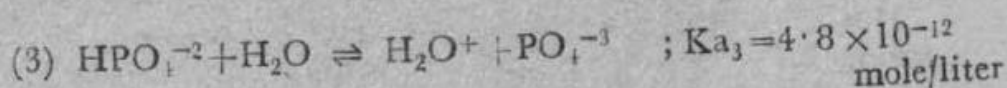
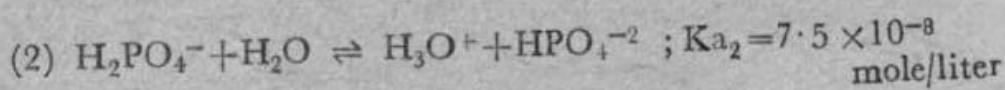
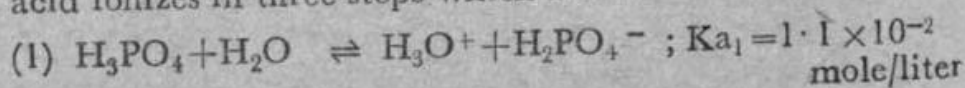
Pure orthophosphoric acid is a deliquescent, white solid with melting point 42°C . It is a triprotic acid and is assigned the following electronic configuration :



It may be noted carefully that the hydrogen atoms in —OH groups are ionizable and therefore acidic, but the P—H bonds in phosphorus acids have reducing, not acidic properties.

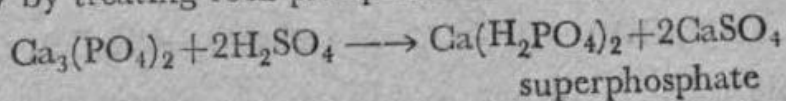
The PO_4^{3-} ion is tetrahedral in structure (compare SO_4^{2-} and CrO_4^{2-}).

The acid ionizes in three steps which are :

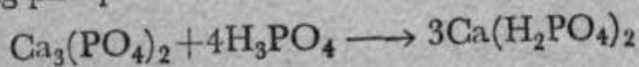


The first ionization constant shows that the ortho phosphoric acid is only a moderately strong acid. As mentioned earlier, it can form three series of salts. *e.g.* NaH_2PO_4 , Na_2HPO_4 and Na_3PO_4 . Sodium dihydrogen phosphate, NaH_2PO_4 is weakly acidic. It is used in baking powder. Disodium phosphate, Na_2HPO_4 , is slightly basic. Trisodium phosphate, Na_3PO_4 , also called the normal sodium phosphate is strongly basic. It is used extensively as a water softener (for treating boiler water) and as a cleansing agent.

Phosphates are valuable fertilizers. The presence of phosphorus in soils is vital for successful plant propagation. One of the most important phosphorus fertilizers is "*superphosphate*", a mixture of calcium dihydrogen phosphate and calcium sulphate. This fertilizer is produced industrially by treating rock phosphate with sulphuric acid :



Since rock phosphate, being too insoluble, cannot serve as an effective source of phosphorus for plants, it is therefore converted into the more soluble form, $\text{Ca}(\text{H}_2\text{PO}_4)_2$. Sometimes, a more effective fertilizer is made by treating phosphate rock with phosphoric acid :



The product is called "*triple phosphate*" and is much richer in phosphorus than the "*superphosphate*".

Fixation of Nitrogen : Animals and plants require nitrogen in order to maintain life. Since they cannot use free nitrogen, they get their supply in the form of nitrogen compounds. The conversion of

chemically unreactive elementary nitrogen into more reactive compounds is called '*nitrogen fixation*'.

Nitrogen compounds are essential to all living organisms for the formation of proteins, which are complicated organic compounds containing carbon, hydrogen, oxygen, nitrogen, and sometimes phosphorus and sulphur. Animals must take proteins directly, as the body is incapable of building up proteins from other nitrogen compounds. On the other hand plants can synthesize proteins from ammonium or nitrate salts, which they derive from the soil. The soil gets nitrogen compounds from the decay of plants, leaves and other organic matter.

Methods for the fixation of nitrogen may be divided into two groups : (1) natural fixation, and (2) artificial fixation.

Natural Fixation: 1. Certain plants such as peas, beans, alfalfa, called *legumes*, maintain a co-operative relationship with certain kinds of nitrogen-fixing bacteria. These bacteria, which are found on the root nodules of the leguminous plants, are able to absorb free nitrogen directly from the atmosphere and convert it into nitrogen compounds.

2. Another method of replenishing the supply of nitrogen compounds in the soil is based on electrical discharges of lightening, which cause the nitrogen and oxygen of the atmosphere to unite. The oxides of nitrogen, thus produced, combine with moisture in the air to form nitrous and nitric acids which are carried down to the soil by rain.

Artificial Fixation : The important methods for artificial fixation of nitrogen are (1) the Haber ; (2) the Birkeland-Eyde ; and (3) the Cyanamide. These processes have already been mentioned in this chapter.

Nitrogen Cycle : Since nitrogen is continually being fixed from the atmosphere by both natural and artificial processes, it may appear as if the supply of nitrogen in the air is decreasing. But this is not true. The percentage of nitrogen in the atmosphere remains almost constant because a balance between free and combined nitrogen is maintained owing to the decomposition of nitrogen compounds, giving elemental nitrogen.

The circulation of nitrogen, from the air to chemical compounds which can be absorbed by plants, then to plant and animal proteins,

and finally back to nitrogen compounds or to free nitrogen, is called the "nitrogen cycle".

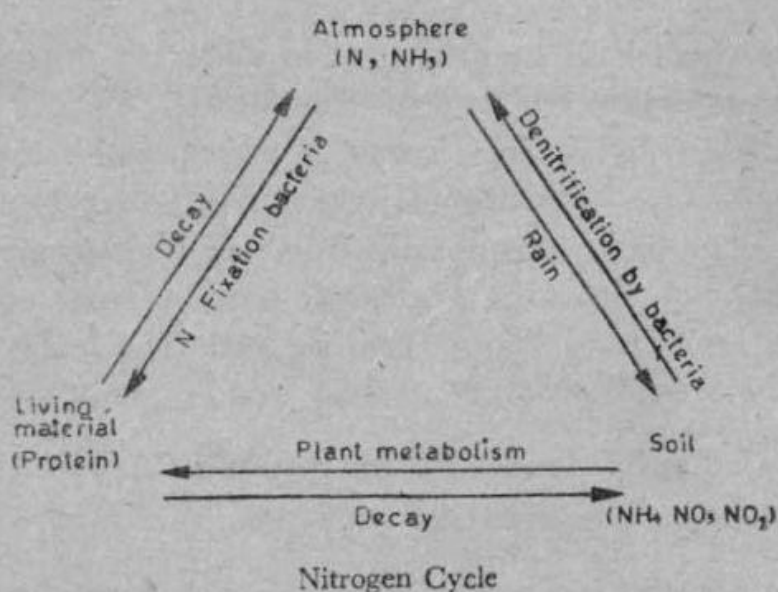
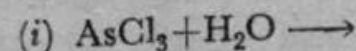
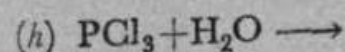
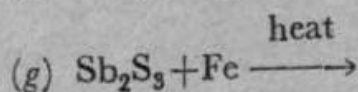
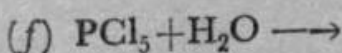
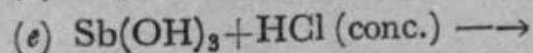
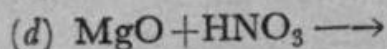
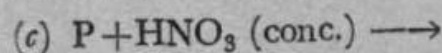
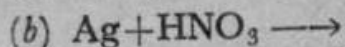
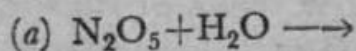


Fig. 6.3

Questions

1. Show the electronic structures of the following :
 $N_2, NH_3, NH_4^+, N_2O, NO, HNO_3, NO_2^-$.

2. Complete and balance the following :



3. Why does elemental nitrogen show relative chemical inertness?

4. Draw the geometrical structures of (a) PH_3 , (b) PCl_5 and (c) PO_4^{-3} .

5. Elemental phosphorus can be prepared by heating rock phosphate with sand and carbon in an electric furnace.
 - (a) Write an equation of the chemical reaction involved in the above process.
 - (b) Calculate the amount of rock phosphate required to obtain 10 grams of phosphorus.
(Answer : 50 g)
 6. Compare NH_3 and PH_3 in regard to :
 - (i) boiling point,
 - (ii) solubility in water,
 - (iii) basicity.
 7. Write equations for the thermal decomposition of the following :—
 NH_4NO_2 , NH_4NO_3 , NH_4Cl , $(\text{NH}_4)_2\text{CO}_3$.
 8. With the help of equations, show that :
 - (a) HNO_3 acts as an acid.
 - (b) HNO_3 acts as an oxidizing agent.
 - (c) NH_3 acts as a base.
 - (d) NH_3 acts as a reducing agent.
 9. Show, by electronic formulas, the structure of H_3PO_4 and H_3PO_3 and account for the difference between these two acids.
 10. Calculate the weight of ammonia that can be obtained from 10 grams of $(\text{NH}_4)_3\text{PO}_4$.
(Answer : 3.42 g)
 11. You are provided with a bottle of 60% HNO_3 having specific gravity of 1.40. Calculate and explain how you would prepare one liter of 0.1N HNO_3 .
(Ans. 7.5 ml of the given acid to be diluted to 1 liter).
 12. What is meant by "fixation of nitrogen"?
 13. Discuss the importance of nitrogen cycle with special reference to the chemical changes which a nitrogen atom undergoes during the cycle.
-

CHAPTER 7

Group VI

THE OXYGEN FAMILY

Group VI comprises of oxygen (O), sulphur (S), selenium (Se), tellurium (Te), and polonium (Po). The last named element occurs naturally in pitchblende which is a radioactive mineral of uranium. Polonium is a disintegration product of radium and is radioactive. It resembles tellurium in its chemical properties. In this chapter we shall not discuss this element in detail.

General Characteristics : Some of the physical properties are listed in table 7.1. The elements in this group have a common s^2p^4 configuration in their valence shells and are thus two electrons short of the next noble gas electronic structures. They can attain noble gas (s^2p^6) electronic configurations in two ways: (1) by gaining two electrons thus forming divalent anions, e.g. O^{-2} and S^{-2} ; (2) by sharing two electrons thus forming two covalent bonds, e.g., H_2O , Cl_2O , H_2S , SCl_2 , CO_2 , OF_2 .

When bonded to a more electropositive element, e.g., in H_2O and H_2S , all the elements of group VI show an oxidation state of -2 ; but when combined with a more electronegative element, for instance in OF_2 and SCl_2 , they exhibit $+2$ oxidation state. The most common oxidation states are $+4$ and $+6$.

There is a general decrease in electronegativity down the group. Thus as the atomic number increases, the electropositive character of the elements also increases. The first four elements are non-metallic in character and are called the *chalcogens* or ore-forming elements, because many metal ores are either oxides or sulphides. Oxygen and sulphur are distinctly non-metals; selenium and tellurium show some metallic properties, and polonium is distinctly a metal.

The relatively high values of ionization potentials show that it is fairly difficult to detach an electron from each atom. It means that metallic character would be lacking. As the size of the atom increases down the group, the first ionization potential decreases correspondingly. It means that the electrons are less firmly bound in larger atoms and metallic character is encountered.

Table 7.1
SOME PHYSICAL PROPERTIES OF GROUP VI ELEMENTS

Symbol	At. No.	Electronic configuration	Atomic radius (Å°)	Melting point (°C)	Boiling point (°C)	First ionization potential (e. v.)	Electro- negativities
O	8	(He) $2s^2 2p^4$	0.74	-219	-183	13.61	3.5
S	16	(Ne) $3s^2 3p^4$	1.04	119	444.6	10.36	2.5
Se	34	(Ar) $3d^{10} 4s^2 4p^4$	1.17	217.4	685	9.75	2.4
Te	52	(Kr) $4d^{10} 5s^2 5p^4$	1.37	450	1390	9.01	2.1
Po	84	(Xe) $4f^{14} 5d^{10} 6s^2 6p^4$	1.52	..	..	8.43	2.0

Oxygen stands apart from other members of the group. It is a diatomic gas at room temperature whereas the rest of the elements are solids and have more complex molecules. Oxygen is never more than divalent as its second (valence) shell is restricted to a maximum of eight electrons. However, the valence shells of sulphur, selenium and tellurium can accommodate more than eight electrons because of the availability of *d* orbitals, and we find compounds in which these elements are linked by single covalent bonds to 4 or 6 groups.

Sulphur, selenium and tellurium combine with oxygen to form typical tetravalent compounds but with fluorine they form hexavalent compounds, *e.g.* SF_6 . In passing down the group, the higher oxidation states become less stable. The compounds with +4 oxidation state show both oxidizing and reducing properties, but those with +6 state are only oxidizing. These compounds are volatile and are typically covalent.

Oxygen differs in chemical behaviour from the rest of the group because (1) it is much more electronegative, and (2) it is unable to hold more than eight electrons in the valence shell.

ELEMENTS

OCCURRENCE

Oxygen, the most abundant of all the elements, occurs free in the atmosphere (23% by weight, 21% by volume). In the combined form, it makes up about 50% by weight of earth's crust; as water it comprises 89% of the oceans. Oxygen is a constituent of all living matter, occurring in carbohydrates, fats, proteins, etc.

Sulphur, which constitutes about 0.05% of the earth's crust, occurs free in nature. In combination, it is found as metal sulphides (*e.g.* Galena (PbS), Zinc blende (ZnS), Iron pyrites (FeS_2), and metal sulphates (*e.g.* barytes, (BaSO_4) , gypsum, $(\text{CaSO}_4 \cdot 2\text{H}_2\text{O})$, and epsom salt $(\text{MgSO}_4 \cdot 7\text{H}_2\text{O})$).

Selenium and Tellurium are very rare and are found as selenides and tellurides of heavy metals. They are generally associated with sulphide ores.

PREPARATION

Oxygen is prepared on an industrial scale by the fractional distillation of liquid air. The nitrogen boils out at a lower temperature than oxygen. The remaining liquid is almost pure oxygen. Pure oxygen can be obtained on a commercial scale by the electrolysis of

water containing sulphuric acid or sodium hydroxide. In the laboratory oxygen is usually made by heating a mixture of potassium chlorate, KClO_3 , with manganese dioxide, MnO_2 , as a catalyst.

Sulphur is brought to the surface in the molten form by first forcing down water at a temperature of 170°C and a pressure of 100 lb. per sq. in. and then pumping down hot compressed air.

Selenium and Tellurium are obtained as by-products in various industrial processes such as electrolytic refining of copper and lead.

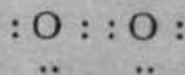
ALLOTROPY

As discussed in chapter 5, "allotropy is a property of certain elements to exist in more than one form due to the rearrangement of the atoms, or molecules."

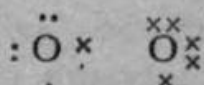
All the elements in this group exhibit allotropy. Oxygen occurs as two non-metallic forms, O_2 and O_3 (Ozone). Sulphur has two well-known crystalline forms : α or rhombic and β or monoclinic. The former is stable at room temperature, while the latter above 95.5°C . Plastic or amorphous sulphur can be obtained by pouring molten sulphur into water. All these forms of sulphur are non-metallic in character. Selenium exists as a non-metallic form (red) and a metallic form (grey). Tellurium has also two allotropic forms : metallic and non-metallic, the former being more stable than the latter. Thus, as explained earlier, there is a gradual increase in metallic character down the group.

MOLECULAR STRUCTURE

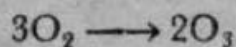
Oxygen exists as discrete molecules (O_2) in the gaseous, liquid and solid states. At high temperatures sulphur, selenium and tellurium vapours also contain diatomic molecules. Oxygen is paramagnetic, *i.e.* when liquid, it is attracted by a magnet. Thus oxygen molecules have unpaired electrons. Its electronic structure cannot be, written as :



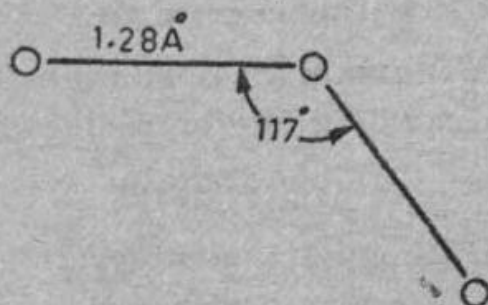
because all the electrons are paired and the molecule should be diamagnetic. The correct formula may be written as



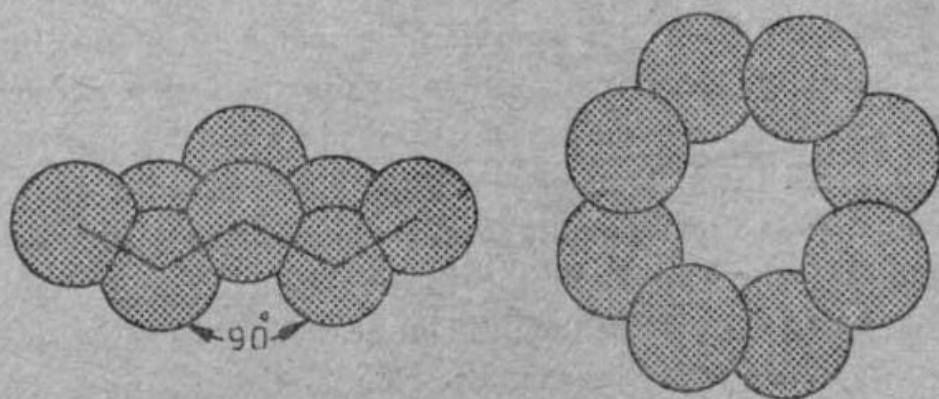
Oxygen, when subjected to an electrical discharge, is converted to ozone :



Ozone decomposes slowly to oxygen. It is an extremely powerful oxidizing agent, next only to fluorine, and reacts much more readily than oxygen. The ozone molecule is diamagnetic and angular in structure. Both the oxygen to oxygen bonds have same length (1.27°A) and bond angle of 119.5° .



Sulphur and selenium exist as S_8 and Se_8 molecules at room temperature and they have a puckered ring structure.



Structure of sulphur (S_8) molecules

HYDRIDES

The general formula for the hydrides is H_2X in which the elements of group VI show an oxidation state of -2 . All the five elements form volatile bivalent hydrides H_2O , H_2S , H_2Se , H_2Te and H_2Po . Hydrogen sulphide, selenide and telluride are easily obtained by the action of dilute non-oxidizing acids on metal sulphides, selenides or tellurides. Thus, hydrogen sulphide is generally prepared in the laboratory by the reaction between iron II sulphide and hydrochloric acid :



H_2S , H_2Se and H_2Te are colourless, evil-smelling and poisonous gases. In the gaseous, liquid and solid states, these hydrides occur as covalent molecules and resemble water structurally.

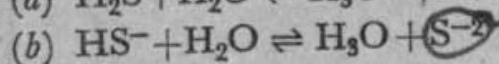
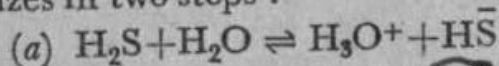
Some important physical properties of the group VI hydrides are given in table 7.2.

Table 7.2
PHYSICAL PROPERTIES OF THE GROUP VI HYDRIDES

Hydride	M.P. (°C)	B.P. (°C)	Heat of formation ΔH_f at 20°C (kcal/mole)	Heat of vaporization ΔH_v (kcal/mole)	Acidity constant (K _a)
H ₂ O	0.0	100.0	-68.35	9.715	1×10^{-14}
H ₂ S	-85.6	-60.75	-4.82	4.463	1×10^{-7}
H ₂ Se	-60.4	-41.5	+18.50	4.75	2×10^{-14}
H ₂ Te	-51.0	-1.8	+34.20	5.7	2×10^{-3}

As the electronegativity of the elements down the group decreases so does the polarity of the molecules. In the case of water, strong hydrogen bonding exists between the molecules in the solid and liquid state because of the great electronegativity of oxygen. Consequently the melting point, boiling point and heat of vaporization of water are much greater than for hydrogen sulphide.

The acidity constants of the hydrides increase down the group. The values show that they act as weak dibasic acids in water. Thus, H_2S ionizes in two steps :

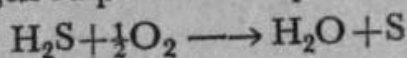


The reducing strength of the hydrides increases down the group. This trend would be expected from the decreasing heat of formation in the molecules. It may be noted that the stability of a molecule with respect to decomposition to the elements generally increases with its heat of formation. As can be seen from Table 7.2, H_2S is stable whereas H_2Se and H_2Te decompose slowly into elements at room temperature. The reducing power of these hydrides increases as their instability increases down the group. In other words the reducing strength varies inversely with the strength of the bond between hydrogen and the group VI elements. One can thus predict on the basis of the heat of formation that water is the poorest reducing agent of these hydrides which is true.

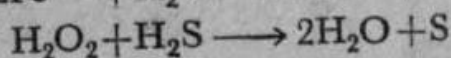
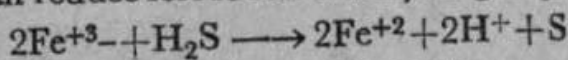
Water being extremely poor reductant, reacts with powerful oxidizing agents such as fluorine, chlorine and bromine *e.g.*,



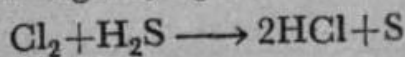
Hydrogen sulphide is a much stronger reducing agent than water. Oxygen oxidizes hydrogen sulphide to sulphur.



Hydrogen sulphide can reduce ferric ion and hydrogen peroxide :

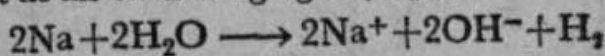


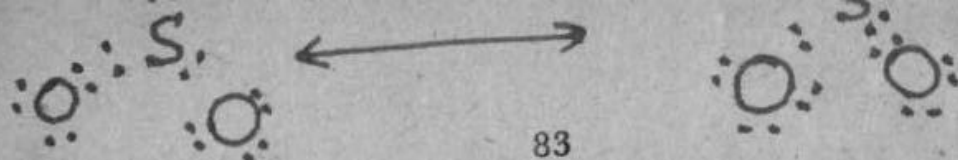
It also reduces all of the halogens, *e.g.*,



Hydrogen selenide and hydrogen telluride are even stronger reducing agents than hydrogen sulphide.

Water can also act as an oxidizing agent, *e.g.*,

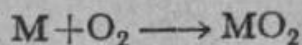




OXIDES

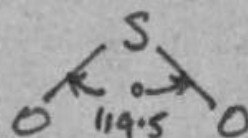
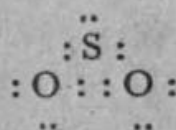
The elements of group VI form a wide range of oxides. The important oxides are the dioxides, MO_2 , in which an oxidation state of +4 is shown, and the trioxides, MO_3 , in which +6 oxidation state is exhibited.

Dioxides : The dioxides of sulphur, selenium, tellurium and polonium are obtained by burning the elements in air.



SO_2 is a colourless, pungent gas. It exists as discrete molecules in the gaseous, liquid and solid states. The molecule is depicted by the following structure :

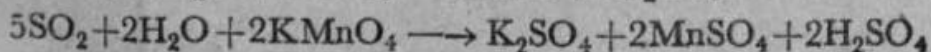
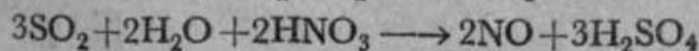
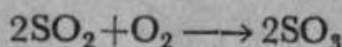
Electronic structure of SO_2



SO_2 is an angular molecule having a bond angle of 119.5° (compare ozone). SeO_2 is a white, volatile solid which forms weakly bonded polymeric chains. In the gas phase, it has the same structure as SO_2 . TeO_2 is a white, non-volatile solid which crystallizes in two ionic forms. The dioxides are extremely stable towards heat.

The solubility of these oxides in water decreases on descending the Group. Sulphur dioxide dissolves in water, but the resultant sulphurous acid, H_2SO_3 , cannot be isolated. Selenium dioxide yields selenious acid, H_2SeO_3 , which can be separated in a crystalline form. Tellurium dioxide is almost insoluble in water. However, it dissolves in alkali to give tellurides and in acid to form basic salts. Thus tellurium shows amphoteric character. As usual, the increase in basic character is illustrated down the group.

Sulphur dioxide is a good reducing agent, as is shown by the following reactions :

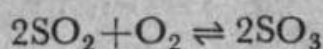


It may be noted that selenium dioxide, in contrast to sulphur dioxide, is a strong oxidizing agent.

Sulphur dioxide has commercial importance as it is used to produce sulphur trioxide, SO_3 , for the manufacture of sulphuric acid. It is also used as a bleaching agent for paper, straw, silk and wool. The

bleaching action is attributed to its reducing property. Sulphur dioxide can be employed as a refrigerant. Since the gas kills fungi and bacteria, it finds applications in the preservation of fruits.

Trioxides : Sulphur trioxide, SO_3 , is the only important trioxide. It is prepared by the direct oxidation of sulphur dioxide by oxygen. The reaction is slow at room temperature and is carried out industrially at temperatures ranging from 400 to 450°C, in the presence of a catalyst such as finely divided platinum metal or vanadium pentoxide, V_2O_5 .



This reaction is an important step in the manufacture of sulphuric acid.

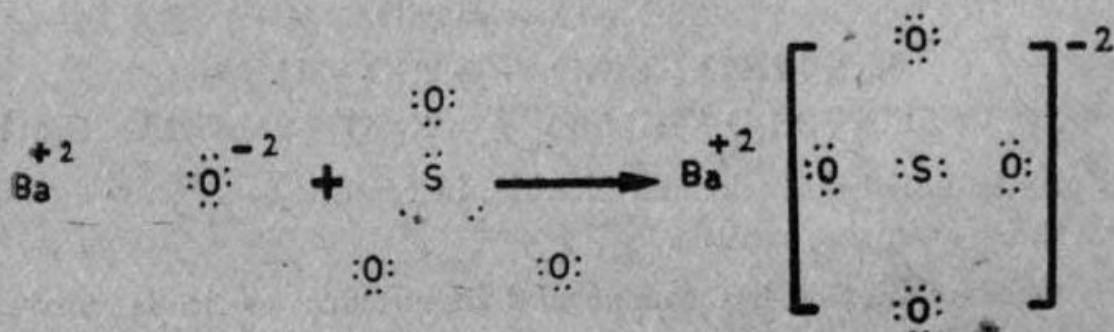
Sulphur trioxide is a volatile white solid which exists in three distinct allotropic forms. In the gas phase, the SO_3 molecule has the structure of an equilateral triangle with sulphur at the centre and oxygen atoms at the corners. The molecule is planar, all the O—S bond angles being 120°.



It may be pointed out that the S—O bond lengths are all equal and shorter than single S—O bonds, thus showing a partly double bond character.

Sulphur trioxide is highly reactive because of the presence of double bonds. It is the anhydride of sulphuric acid, H_2SO_4 , and reacts vigorously with water to form the acid. The reaction is highly exothermic. This is a typical reaction in which SO_3 acts as a strong Lewis acid. Sulphur trioxide also combines with concentrated sulphuric acid (98%) to give *fuming* sulphuric acid (*oleum*). When the molecules of SO_3 and H_2SO_4 are present in the ratio of 1 : 1, the product is disulphuric acid, $\text{H}_2\text{S}_2\text{O}_7$ (pyrosulphuric acid). Further addition of SO_3 yields a series of polysulphuric acids.

Sulphur trioxide combines violently with basic oxides giving sulphates :



It may be of interest to note that a geometrical change takes place in

the reaction mentioned above. Whereas SO_3 molecule has a plane triangular structure, the SO_4^{-2} ion is tetrahedral.

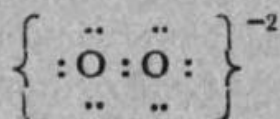
Sulphur trioxide is a strong oxidizing agent, especially at high temperatures. It oxidizes chlorides, bromides, and iodides of both metals and non-metals, liberating free halogens and is itself reduced to SO_2 .

Selenium trioxide, SeO_3 , is prepared by dehydrating selenic acid, H_2SeO_4 , with phosphorus pentoxide.

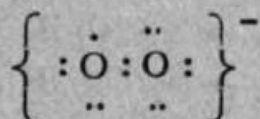
Classification of Oxides : Oxygen can combine, often directly, with all elements except some noble gases. Oxides thus formed, are classified on the basis of their internal structure into the following groups :

Normal Oxides : In these oxides, oxygen has an oxidation number of -2 . They contain only $\text{M}-\text{O}$ bonds where M stands for any element other than oxygen. These bonds may be ionic or covalent, *e.g.* MgO , CO_2 and H_2O .

(2) **Peroxides :** Oxygen has an oxidation state of -1 in them. They contain more oxygen than would be expected from the oxidation number of M . The peroxides involve $\text{O}-\text{O}$ bonds as well as $\text{M}-\text{O}$ bonds but no $\text{M}-\text{M}$ bonds, *e.g.*, H_2O_2 ($\text{H}-\text{O}-\text{O}-\text{H}$) Na_2O_2 and BaO_2 . When treated with water, all peroxides give hydrogen peroxide. It is of interest to note that all metals of groups I and II except beryllium form peroxides. The electronic formula of the peroxide ion O_2^{-2} may be represented as



(3) **Superoxides :** The oxidation number of oxygen in superoxides is $-\frac{1}{2}$. They also contain more oxygen than would be expected, and are related to peroxides. All the metals of Group I except lithium form superoxides *e.g.*, KO_2 . The superoxide ion, O_2^- , contains an unpaired electron which makes it paramagnetic and coloured. Its electronic structure may be written as



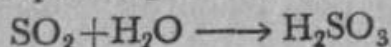
(4) **Suboxides :** They contain less oxygen than would be expected from the oxidation number of M . They involve $\text{M}-\text{M}$ as well as $\text{M}-\text{O}$

bonds but no O—O bonds, *e.g.*, carbon suboxide (a gas), C_3O_2 , $O=C=C=C=O$. The oxidation number of carbon in carbon suboxide is $+1\frac{1}{3}$, whereas that of oxygen is the usual -2 .

1. NORMAL OXIDES

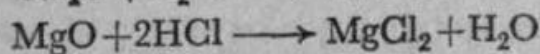
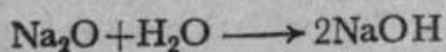
Normal oxides constitute by far the most important class and can be sub-divided into (1) acidic, (2) basic, (3) amphoteric, and (4) neutral, depending on their behaviour with water, acids and alkalis. These oxides, when arranged in a series, show a gradual change from strongly basic to strongly acidic character. This trend is attributed to the increasing electronegativity of the element. It may also be noted that in a series of normal oxides of *different* elements the acidic nature of the oxide increases with the increase in proportion of oxygen, *i.e.* with the increase in oxidation number of the element. This important rule applies also to different oxides of the *same* element. For example, SO_3 is more acidic than SO_2 . Similarly, CrO is basic, Cr_2O_3 amphoteric and CrO_3 strongly acidic.

(a) **Acidic Oxides** : They are generally the oxides of non-metals, *e.g.*, CO_2 , NO_2 , SO_2 , P_4O_{10} . They are soluble in water and react with it forming the corresponding acids, *e.g.*,

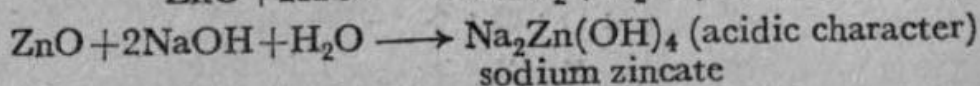
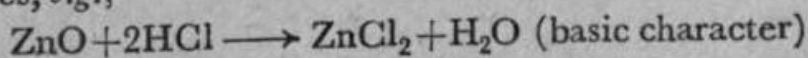


Acidic oxides react with alkalis to give corresponding salts and water. Since these oxides may be obtained from the corresponding acids by the removal of water molecules, they are also called 'anhydrides' of their acids.

(b) **Basic Oxides** : They are oxides of metals. The oxidation number of the metals in these oxides is $+4$ or less. Strongly basic oxides are soluble in water while the rest are insoluble. Soluble oxides give alkalis when dissolved in water. They react with acids to form salts and water, *e.g.*,



(c) **Amphoteric Oxides** : They are the oxides of weak electro-positive metals such as aluminium, zinc and tin. These oxides show both acidic and basic character. They form salts when treated with acids or alkalis, *e.g.*,



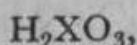
It may be of interest to note that all amphoteric oxides are insoluble in water.

(d) **Neutral Oxides** : They show neither acidic nor basic character, *e.g.* carbon monoxide, CO, nitrous oxide, N₂O, and nitric oxide, NO. They are insoluble in water. Although water is generally considered as a neutral oxide, it should more correctly be treated as an amphoteric hydroxide, H(OH).

OXYACIDS

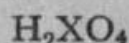
The elements of Group VI form a wide range of oxyacids. Two important series of acids are :

- (1) —ous acids, having the general formula



in which the oxidation state is +4, and

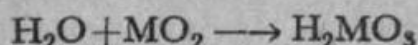
- (2) —ic acids, having the general formula



in which the oxidation state is +6.

The oxyacids of sulphur are more important and more numerous than those of selenium and tellurium. Quite a few of them do not exist as free acids, but their anions and salts are known.

Tetraivalent Oxyacids : These oxyacids are obtained by the reaction of dioxides with water :



They are weak diprotic acids. The acids with their formulas and ionization constants are listed in Table 7.3.

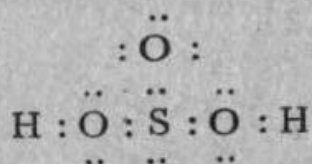
Table 7.3

ACIDITY CONSTANTS OF TETRAVALENT OXYACIDS

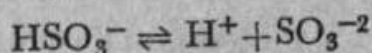
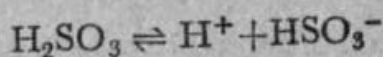
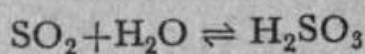
Acid	Formula	K _{a1}	K _{a2}
Sulphurous	H ₂ SO ₃ or SO(OH) ₂	1.3 × 10 ⁻²	5.6 × 10 ⁻⁸
Selenous	H ₂ SeO ₃ or SeO(OH) ₂	2.5 × 10 ⁻³	1 × 10 ⁻⁸
Tellurous	H ₂ TeO ₃ or TeO(OH) ₂	2 × 10 ⁻³	...

It may be noted that no regular trend in acid strength is observed.

As pointed out earlier, sulphurous acid has never been obtained in the free state. Like carbonic acid, H_2CO_3 , it exists only in aqueous solution. The acid may be represented by the electronic formula given below :



When SO_2 is dissolved in water, the following equilibria are established :



The ionization constants at 25°C for the two steps of ionization are given below :

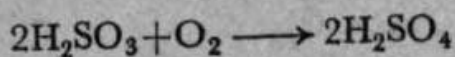
$$K_{a1} = \frac{[\text{H}^+][\text{HSO}_3^-]}{[\text{H}_2\text{SO}_3]} = 1.3 \times 10^{-2} \text{ mole/liter}$$

$$K_{a2} = \frac{[\text{H}^+][\text{SO}_3^{2-}]}{[\text{HSO}_3^-]} = 5.6 \times 10^{-8} \text{ mole/liter}$$

Thus H_2SO_3 ($K_{a1} = 1.3 \times 10^{-2}$) is a stronger acid than H_2CO_3 ($K_{a1} = 4.3 \times 10^{-7}$) and acetic acid, CH_3COOH ($K_a = 1.8 \times 10^{-5}$).

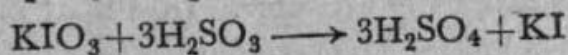
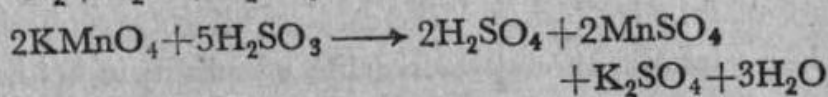
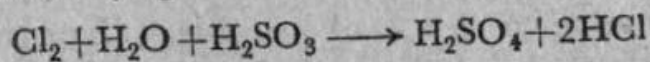
A sulphurous acid solution contains both the acid sulphite ion, HSO_3^- , and the sulphite ion, SO_3^{2-} . Salts containing the former are called acid sulphites or bisulphites, those containing the latter are known as sulphites. The sulphites of alkali metals and ammonium ion are soluble in water, while most other sulphites are insoluble.

Sulphurous acid and solutions of its salts can act both as reducing and oxidizing agents. All of these compounds contains sulphur in the +4 oxidation state, and generally act as reducing agents than as oxidizing agents. These sulphur compounds find many uses on the basis of their reducing property. Solutions of sulphurous acid, sulphites or bisulphites are slowly oxidized to sulphate, SO_4^{2-} , by atmospheric oxygen.

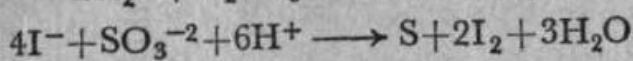
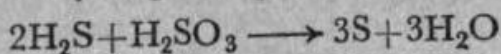


Strong oxidants such as chlorine, potassium permanganate, potassium

dichromate and potassium iodate readily oxidize sulphite ion quantitatively to sulphate ion, *e.g.*

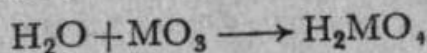


Sulphurous acid shows its oxidizing character only towards strong reducing agents such as hydrogen sulphide and iodide ion, *e.g.*



Unlike sulphurous acid, free selenous acid has been isolated. Free tellurous acid is unknown.

Hexavalent Oxyacids : These oxyacids are obtained by reaction of the trioxides and water :



The acids with their formulas and acidity constants are listed in Table 7.4.

Table 7.4

ACIDITY CONSTANTS OF HEXAVALENT OXYACIDS

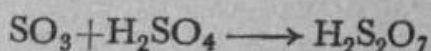
Acid	Formula	K_{a1}	K_{a2}
Sulphuric	H_2SO_4 or $\text{SO}_2(\text{OH})_2$	10^{-9}	10^{-2}
Selenic	H_2SeO_4 or $\text{SeO}_2(\text{OH})_2$	10^{-3}	...
Telluric	H_6TeO_6 or $\text{Te}(\text{OH})_6$	10^{-7}	...

As can be seen from the above table, sulphuric and selenic acids are strong, but telluric acid is a weak diprotic acid. In structure telluric acid differs from the others.

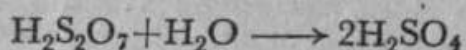
Sulphuric acid, H_2SO_4 , is perhaps the most important of all manufactured chemicals. It is produced commercially by two processes : (1) the *contact process*, and (2) the *lead-chamber process*. Both the processes involve three main steps :

- (i) production of SO_2 ,
- (ii) catalytic oxidation of SO_2 to SO_3 by atmospheric oxygen, and
- (iii) combination of SO_3 with water to form H_2SO_4 .

In the *contact process*, platinum or preferably vanadium pent-oxide, V_2O_5 , is used as a catalyst. The sulphur dioxide used in the process must be very pure since even small quantities of impurities such as compounds of arsenic, "poison" the catalyst, thereby rendering it ineffective. Sulphur trioxide, though anhydride of sulphuric acid, is not dissolved directly in water to get the acid as it forms a mist of H_2SO_4 which is absorbed slowly in the liquid water. In actual practice, it is passed into 98% sulphuric acid. The reaction proceeds readily and smoothly, yielding pyrosulphuric acid, $H_2S_2O_7$.

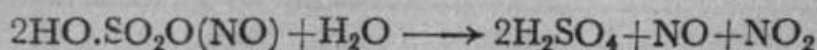
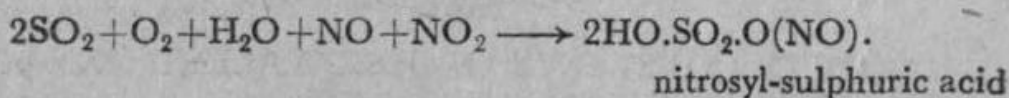


Pyrosulphuric acid is then converted into sulphuric acid of the desired concentration by adding water.



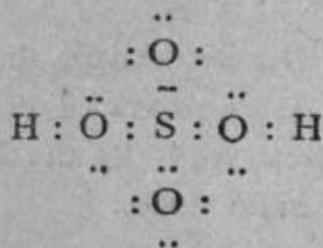
Sulphuric acid produced by this method may be 100% pure acid.

In the *lead-chamber process*, the catalyst is a gas, nitric oxide, NO. Hot SO_2 is fed into lead-lined chambers and is made to react with atmospheric oxygen and steam in the presence of NO and NO_2 . The mechanism of the reaction is not fully understood. However, the reactions may be represented by the following equations :



The oxides of nitrogen, which are recovered unchanged, are reused in the process. In contrast to the contact process, this process does not require pure SO_2 . The acid produced by the lead-chamber process contains 62–77% H_2SO_4 .

Pure (100%) sulphuric acid, which is a covalent compound may be represented by the following electronic structure :



Like the sulphate ions the H_2SO_4 molecule has a tetrahedral structure. Pure H_2SO_4 is a colourless, viscous liquid (density 1.85) which freezes at $10.37^\circ C$ and boils at about $290^\circ C$ with decomposition into SO_3 and

water. Ordinary concentrated sulphuric acid (98% H_2SO_4 and 2% H_2O) is 18 molar and has density of 1.84.

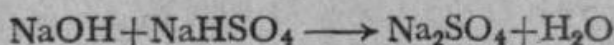
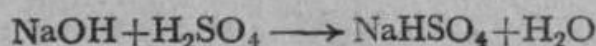
Sulphuric acid is a diprotic acid and forms two ionic species in aqueous solution, the bisulphate ion HSO_4^- , and the sulphate ion SO_4^{2-} :



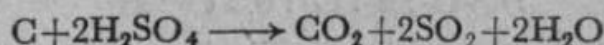
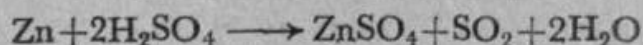
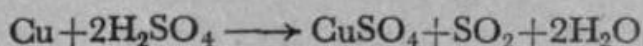
In dilute solutions, the first stage of ionization is almost complete. However, the second ionization occurs relatively to a small extent, the acidity constant of the HSO_4^- ion being approximately 10^{-2} mole/liter 25°C . Thus the bisulphate ion is itself a moderately strong acid and the solutions of bisulphate compounds are acidic, whereas those of sulphate compounds are almost neutral. All bisulphates and most of the sulphates, except those of calcium, strontium, barium and lead, are soluble in water.

Sulphuric acid is a very corrosive substance. It exhibits four distinct sets of chemical properties, i.e., it can act (1) as a strong diprotic acid, (2) as an oxidizing agent, (3) as a dehydrating agent, (4) as a sulphonating agent.

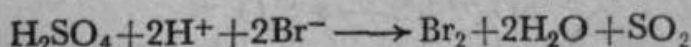
Dilute sulphuric acid shows typical acid reactions. It neutralizes bases to form salts, e.g.,



Hot concentrated sulphuric acid is a quite strong oxidizing agent. It can oxidize both metals and non-metals, e.g.,



It may be of interest to notice that copper is below and zinc is above hydrogen in the electrochemical series. It cannot oxidize chloride or fluoride ions but it does oxidize bromide and iodide ions, liberating free halogens:



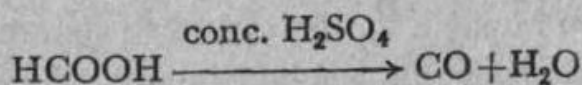
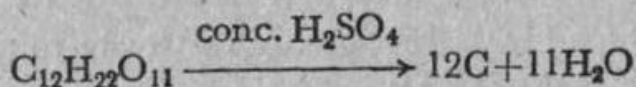
It may be noted that the reactions in which H_2SO_4 acts as an oxidant involve the reduction of sulphur from its oxidation state of +6 to +4.

Dilute H_2SO_4 can oxidize metals such as magnesium and zinc, with the liberation of hydrogen, *e.g.*,



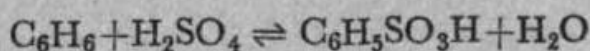
In this reaction the oxidation state of sulphur remains unchanged.

Concentrated sulphuric acid is a powerful dehydrating agent as it has a great tendency to combine with water. It can remove water molecules from sugar ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) and formic acid (HCOOH) :

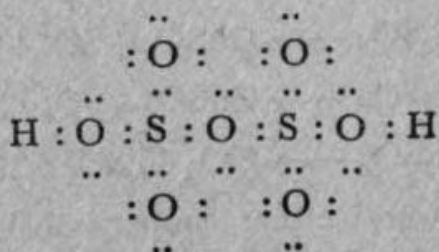


In the case of sugar a charred mass of free carbon is left. The charring of wood, paper, cotton and wool by concentrated H_2SO_4 results from the same dehydrating property.

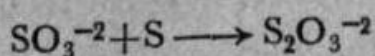
Benzene, when refluxed with 100% H_2SO_4 , gives benzene sulphonic acid :



Other important oxyacids containing sulphur in the +6 oxidation state are pyrosulphuric acid, $\text{H}_2\text{S}_2\text{O}_7$, and peroxy-disulphuric acid, $\text{H}_2\text{S}_2\text{O}_8$. The preparation of the pyro acid, also known as *oleum* or *fuming sulphuric acid*, has already been given. The electronic formula of pyrosulphuric acid is given below :

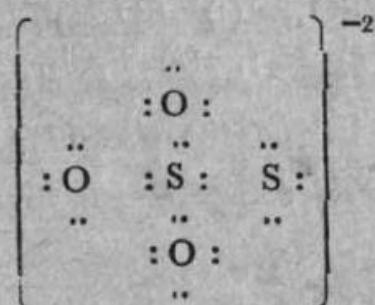


Thio acids : When a solution of a metal sulphite is boiled with S the following reaction occurs :



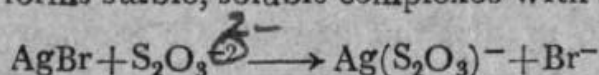
Compounds containing the $\text{S}_2\text{O}_3^{-2}$ radical are called thiosulphates. The thiosulphate ion ($\text{S}_2\text{O}_3^{-2}$) is similar to the sulphate ion, SO_4^{-2} , in

structure; the one oxygen atom of tetrahedral sulphate ion having been replaced by one sulphur atom :

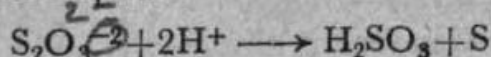


In the $\text{S}_2\text{O}_3^{-2}$ the central S atom is in a +6 oxidation state, whereas the other sulphur atom has an oxidation number of -2.

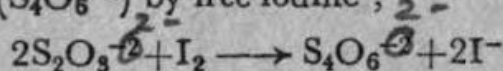
Sodium salt is the most common thiosulphate which crystallizes from solution as $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ in monoclinic crystals. "Hypo", as it is commonly called, is extensively used in photography to remove unreacted silver bromide (AgBr) from the photographic films. The thiosulphate ion forms stable, soluble complexes with silver ion, e.g.,



In acidic solutions, the thiosulphate ion decomposes to give sulphurous acid and free sulphur :



The thiosulphate ion is a good reductant and can be oxidized to the tetrathionate ion ($\text{S}_4\text{O}_6^{-2}$) by free iodine ;



This reaction is rapid and is employed for the quantitative determination of iodine.

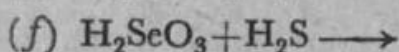
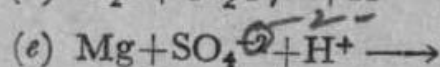
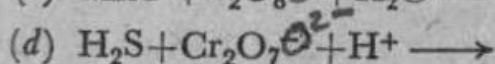
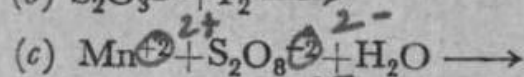
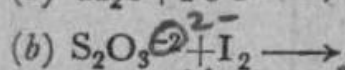
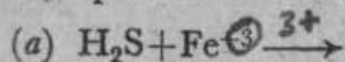
Questions

1. Compare the elements of Group VI in regard to (a) electronic configurations, (b) electropositive character, (c) melting and boiling points, (d) heats of vaporization, (e) electronegativity, and (f) their tendency to form dinegative ions.
2. What is allotropy? Discuss briefly the allotropic modifications of the members of the oxygen family. Is O_3 an allotropic form of oxygen?

3. Depict the electronic formulas and suggest the geometry of the following :

(a) SO_2 , (b) SO_3 , (c) SO_4^{--} , (d) $\text{S}_2\text{O}_3^{--}$, (e) $\text{S}_2\text{O}_7^{--}$,
 (f) $\text{S}_2\text{O}_8^{--}$, (g) H_2S , (h) S_2Cl_2 , (i) SeCl_4 , and (j) SF_6 .

4. Complete and balance the following equations :

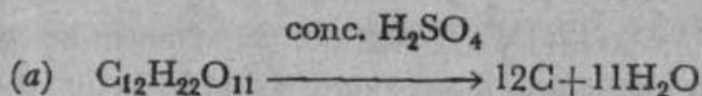


Pick up the oxidizing and the reducing agents in each of the above equations.

5. Discuss the stereochemistry of the water molecule. How would you predict the approximate geometry on the basis of atomic orbitals employed in the formation of the molecule?
6. Compare and contrast water with hydrogen sulphide with respect to their physical properties, acidity and redox properties. Give explanation for the differences.
7. Liquid hydrogen sulphide is a much poor solvent for salts than is water. Explain.
8. Show that H_2S :
- is an acid,
 - is a reducing agent, and
 - contains sulphur.
9. Calculate the amount of sulphur required to produce 101.605 tons of 98% (by weight) sulphuric acid. (Answer : 32.513 tons).
10. Sulphur dioxide acts both as an oxidant and a reductant, but hydrogen sulphide acts only as a reductant. Explain and give equations to illustrate your answer.
11. Ordinary concentrated sulphuric acid has a molarity of 18 :
- Calculate the volume of the acid required to prepare 2 liters of 0.1N H_2SO_4 .
 (Ans. 5.55 ml)

(b) Calculate the weight in grams of the H_2SO_4 in 10 liters of this acid. (Ans. 17640 g)

12. State the different aspects of the properties of sulphuric acid depicted in the following chemical reactions :



13. Why can't sulphuric acid be prepared by treating a metal sulphate with an acid?
14. Barium sulphite is soluble in a dilute mineral acid whereas barium sulphate is insoluble. Why?
15. Arrange the following oxides in order of increasing acid strength CO_2 , K_2O , H_2O , SO_3 , SiO_2 , CaO , N_2O_5 , MgO .
-

CHAPTER 8

THE HALOGENS

Fluorine, chlorine, bromine, and iodine, are known as *halogens*. They occupy a unique position in the periodic table in being the most reactive of the elements known. Due to their extreme reactivity they occur in nature in combination with other elements and never in the free state. They are placed in group VII of the periodic table because their electronic configuration reveals that they contain seven electrons in their outermost orbit. This means that halogens possess one less electron than the relatively unreactive noble gases (Ne, Ar, Kr, Xe) which have eight electrons in their outermost orbit. The electronic configurations of fluorine (F), chlorine (Cl), bromine (Br) and iodine (I) are given below (Table 8.1).

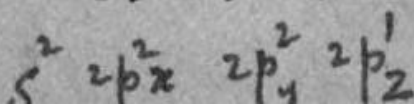
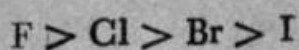
Table 8.1

Atomic Number	Element	Electronic Configuration
9	F	[He]Core + $2s^2 2p^5$
17	Cl	[Ne]Core + $3s^2 3p^5$
35	Br	[Ar]Core + $3d^{10} 4s^2 4p^5$
53	I	[Kr]Core + $4d^{10} 5s^2 5p^5$

It can be seen from the above table that each member of the halogen family has the end configuration of $s^2 p^5$. The integers 2, 3, 4 and 5 before $s^2 p^5$ arrangement for fluorine, chlorine, bromine and iodine respectively indicate their principal quantum numbers. In detail the arrangement of electrons for halogens (for the outer orbits) may be written as :



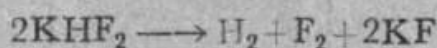
Due to one unshared electron in one of the p orbitals, halogens behave as monovalent elements. They are highly electronegative (tendency to acquire electron) and their electronegativity decreases with the rise in the atomic number as shown :



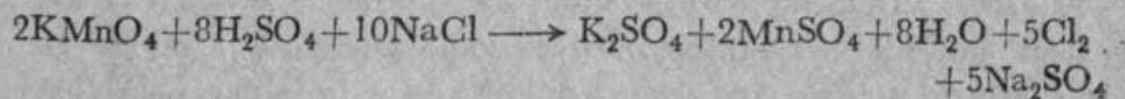
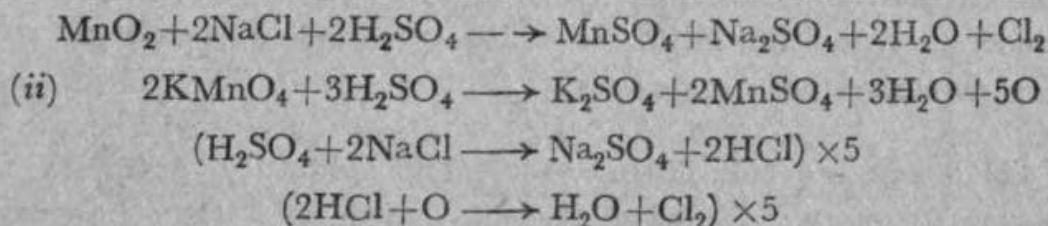
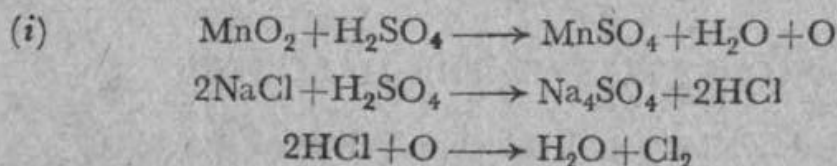
OCCURRENCE AND PREPARATION

The halogens are not found free in nature but occur as halide salts, the most abundant being chlorides and fluorides. Fluorine is found in nature as fluorspar (CaF_2); cryolite, Na_3AlF_6 ; and fluorapatite, $\text{Ca}_3(\text{PO}_4)_2$, CaF_2 . Chlorine occurs in nature mainly as sodium chloride, NaCl . The salt can be recovered from oceans or from salt mines. There are large deposits of sodium chloride in the Khewra salt mines in the Punjab. The other two halogens namely Br and I are relatively less abundant. The bromides of Na, K and Mg are found with NaCl in sea water. NaIO_3 and NaIO_4 are found in Chile as impurities in NaNO_3 .

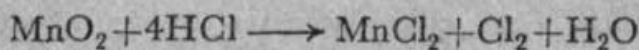
Fluorine is prepared by electrolysis of anhydrous molten potassium hydrogen fluoride KHF_2 . The electrolysis is carried out in a nickel or copper vessel fitted with carbon electrodes.



Chlorine can be prepared in the laboratory by the action of sulphuric acid on sodium chloride in the presence of an oxidizing agent (MnO_2 or KMnO_4).



A simple method for the preparation of chlorine is the reaction between MnO_2 and HCl .



If HBr or HI is used in place of HCl , gaseous bromine or iodine may be obtained.

Chlorine is very important as a bleaching agent, for which large quantities of this gas are used. Chlorine is manufactured on an industrial

scale by the electrolysis of an aqueous solution of NaCl. A typical electric cell used for the preparation of chlorine is shown in Fig. 8.1. Different parts of the cell are labelled in the diagram. It may be noted that NaOH and hydrogen gas are produced as by products.

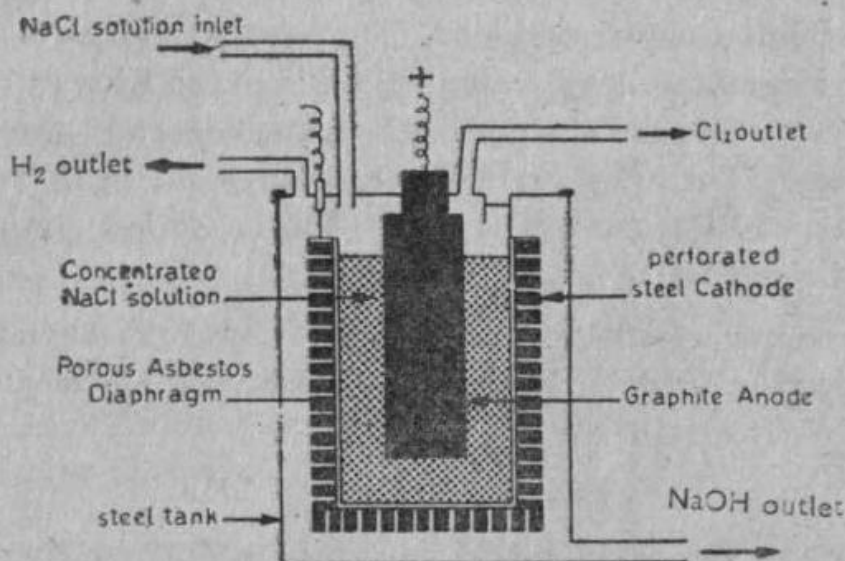


Fig. 8.1 : Nelson Cell

PROPERTIES OF THE HALOGENS

Fluorine (pale yellow) and chlorine (yellowish green) are gases at room temperature. Bromine (orange red) is a fuming liquid and iodine (violet) a low melting solid. It can be seen that the intensity of colour increases with rising atomic weight.

Halogens are soluble in water. The solubility decreases from fluorine to iodine. Fluorine, in fact, decomposes water into oxygen and ozone. Chlorine and bromine are soluble in water to quite an extent and this dissolution involves some chemical reaction. Iodine is sparingly soluble in water but dissolves in other polar solvents such as ethyl alcohol giving brown coloured solution. However, the solubility of iodine in non-polar solvents like carbon tetrachloride, carbon disulphide and chloroform is quite appreciable and the solutions are violet in colour. Aqueous solution of iodine is prepared by dissolving iodine in water in the presence of potassium iodide. The iodide ion changes the iodine to the soluble ion I_3^- . Other physical properties are given in the Table 8.2 below and a discussion concerning some of these follows :

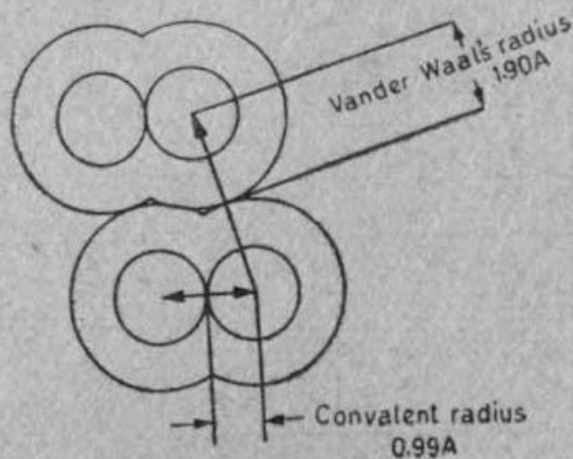
Table 8.2

Halogen, X_2	Covalent radius A°	Van der Waal's radius A°	Ionic radius X^{-1} ion A°	Melting point $^\circ K$ $^\circ C$	Boiling point $^\circ K$ $^\circ C$	Bond energy $kcal/mole$	Dissociation constant at $1000^\circ C$
Fluorine	0.64 0.72	1.35	1.36	-223 55	-188 85	37.7 66	..
Chlorine	0.99	1.80	1.81	-102 172	-35 238.9	57.9 67	1×10^{-8}
Bromine	1.14	1.95	1.95	-7 265.7	59 331.8	46.1 45.5	8×10^{-3}
Iodine	1.33	2.15	2.16	114 337	184 457	36.1 55.0	1×10^{-1}

THE SIZES OF HALOGEN ATOMS AND IONS

It may be seen in the above table that the sizes for different halogens are listed under headings like covalent radius, Van der Waal's radius and ionic radius. These three quantities in fact refer to the sizes of halogen atoms, ions and molecules in different chemical situations.

The first two terms namely covalent radius and Van der Waal's radius are used where two atoms of the same element are combined to give a molecule of that gas. If diatomic molecules of fluorine, chlorine, bromine and iodine are considered, one half of the measured bond distance (internuclear distance) is called the covalent radius. Hence it should be clearly seen that the term covalent radius is used for a situation within one molecule. Half of the internuclear distance between two atoms which touch each other but belong to separate molecules is known as the *Vander Waal's radius or collision radius*. The following Figure (8.2) explains further the difference between the terms covalent radius and Vander Waal's radius.

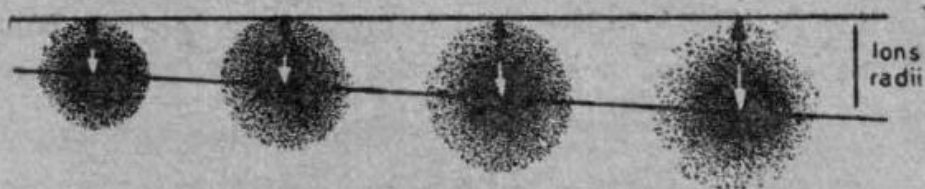


Comparison of covalent radius with Van der Waal's or collision radius for Chlorine.

Fig. 8.2

When effective sizes of the halogens bonded in ionic compounds are required, the halide ions are treated as spheres and their radii are called ionic radii. It can be seen that the values for the Van der Waal's radii of these elements are close to the ionic radii of their ions. On the other hand the values are much larger than the covalent radii. Furthermore the values for covalent, Van der Waal's and ionic radii increase with

increasing atomic weight. The relative sizes of the fluoride, chloride, bromide and iodide ions are pictured in Fig. 8.3.



Comparative ionic radii of the halide ions.

Fig. 8.3

Last column of the table 8.2 contains values of the dissociation constants of the diatomic molecules for halogens. If X is considered to be any halogen, then a reaction of the type below may be described.



The equilibrium constant K may now be defined as

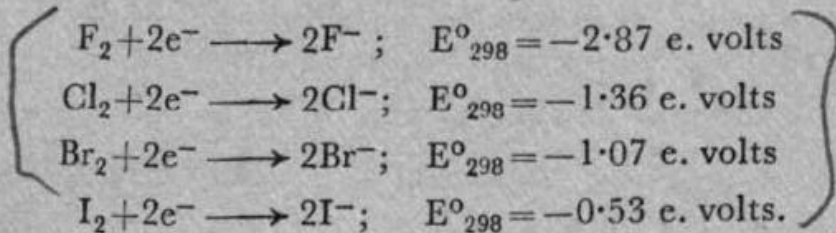
$$K = \frac{[\text{X}]^2}{[\text{X}_2]}$$

where [X] and [X₂] are the partial pressures of X atoms and X₂ molecules. The equilibrium constant increases from chlorine to iodine indicating that the stability of the halogen molecules decreases from chlorine to iodine. This is also indicated by their bond energies given in the table 8.2.

Fluorine behaves differently, and no satisfactory explanation for the unusually low bond energy of fluorine has been given so far.

CHEMICAL PROPERTIES

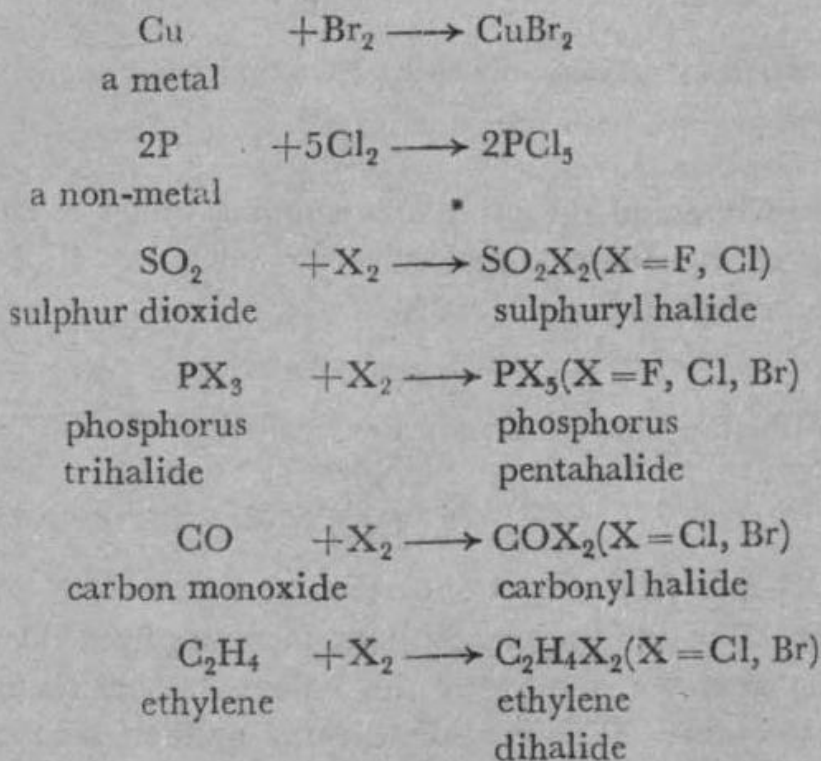
The halogens are extremely reactive because of their ability to acquire one electron (oxidizing ability). Their reduction potentials are given below :



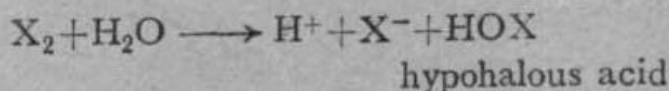
The above figures indicate that fluorine is the strongest oxidant while iodine is very weakly so. It can also be seen that on the basis of their reduction potentials chlorine will displace bromine from bromides and bromine will displace iodine from an iodide, *e.g.*



The halogens also react directly with metals and non-metals. This reaction is more vigorous with fluorine than with chlorine. Similarly bromine is more reactive than iodine. The halogens would also react directly with some molecules of the covalent type. Some of the reactions are shown below :



Fluorine reacts readily with water to form hydrofluoric acid along with other oxidation products such as O_2 and O_3 . Chlorine, bromine and iodine react with water to yield the corresponding hypohalous acids as shown :

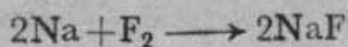


The extent to which this reaction goes with each of the three halogens is indicated by the values of the equilibrium constants of the respective reactions with water.

	K mol ² liter ⁻²
For Chlorine	4.7×10^{-4}
For Br ₂	5.8×10^{-9} 7.2×10^{-9}
For I ₂	3.0×10^{-13} 2.0×10^{-13}

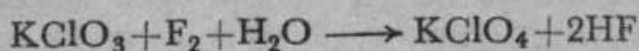
Fluorine being the most reactive of all the halogens, combines with almost all elements except a few.

Alkali and alkaline earth metals catch fire in it. Other metals react with it while hot *i.e.* Zn, Cd etc.

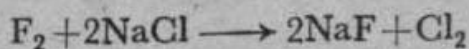


With non-metals it reacts vigorously. It combines with hydrogen even at -250°C or in darkness.

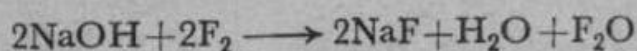
It is a powerful oxidizing agent, thus oxidises potassium chlorate to perchlorate.



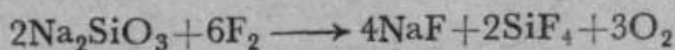
It displaces all the other halogens from their salts.



It reacts with alkalies to form fluorine monoxide.



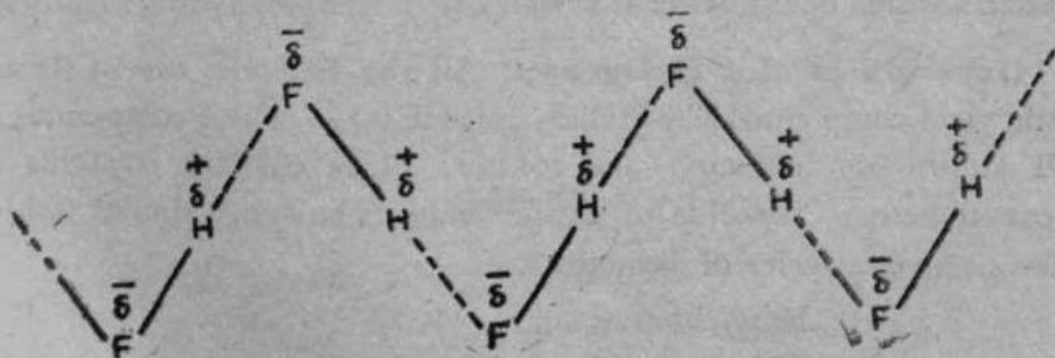
It attacks glass,



COMPOUNDS OF HALOGENS

Hydrogen Halides : All the hydrogen halides, namely, HF, HCl, HBr and HI, are strongly acidic. The acid strength increases from hydrogen fluoride to hydrogen iodide.

As a matter of fact HCl, HBr and HI in a solvent like water are equally strong. This is due to the fact that these compounds are almost completely ionized in water. Only hydrogen fluoride is associated at ordinary temperature by protonic bridges shown below :



This associated structure makes the hydrogen of the hydrogen fluoride less available for a solvent like water.

The ease with which these acids can ionize would also depend upon the strength of the bond between the hydrogen and the halogen. A quantitative estimation of the heats of formation (ΔH_f) for these hydrogen halides is given below :

	HF	HCl	HBr	HI	
ΔH_f	-64.0	-22.06	-8.66	+6.20	kcal/mole

These values indicate that the stability of bonds between hydrogen and respective halides decreases from HF to HI.

Some important properties of hydrogen halides are given in table 8.3.

Table 8.3

8.4

IMPORTANT PROPERTIES OF HYDROGEN HALIDES

Hydrogen halides	M.P. °C	B.P. °C	Percent of dissociation into elements at 1000°C	Percent of ionization 0.1 molar aqueous solution at 18°C
HF	-83.1	19.5	...	10
HCl	-114.8	-84.9	0.014	92
HBr	-86.9	-66.8	0.5	92
HI	-50.7	-35.4	33	92

The unusually high values for the melting point and boiling point of HF are explained in terms of the association occurring between HF molecules which does not occur to that extent in other hydrogen halides.

Oxyacids of the Halogens : All the halogens except fluorine would yield compounds like HClO_3 and HClO_4 . These compounds are well known for chlorine and iodine. Only chlorine oxyacids are discussed here. Oxyacids of iodine would behave in a similar fashion. Chlorine gives a series of oxyacids.

Hypochlorous acid	HClO
Chlorous acid	HClO_2
Chloric acid	HClO_3
Perchloric acid	HClO_4

These acids are unstable and hence difficult to handle in the laboratory. However their aqueous solutions are reasonably stable. The acidity for these acids increases with increasing number of atoms of oxygen. It is found that HClO is a weak acid, HClO_2 is stronger than HClO , HClO_3 is a very strong acid and HClO_4 is probably one of the strongest acids known.

The acid strength in the above cases may be explained by saying that the addition of oxygen atom to the central atom makes the OH bond weaker. Furthermore, it would be seen that the perchlorate and the chlorate ions are more stable than the *hypochlorous* and the *chlorous* ions. This is perhaps due to the spreading of the charge on a bigger ion and thus making it more stable.

STRUCTURE OF THE VARIOUS OXYACIDS OF CHLORINE

Acid	Anions
Hypochlorous acid $\text{H}-\ddot{\text{O}}-\ddot{\text{Cl}}:$	$\left\{ :\ddot{\text{O}}-\ddot{\text{Cl}}: \right\}^-$
Chlorous acid $\text{H}-\ddot{\text{O}}-\ddot{\text{Cl}}-\ddot{\text{O}}:$	$\left\{ :\ddot{\text{O}}-\ddot{\text{Cl}}-\ddot{\text{O}}: \right\}^-$
Chloric acid $\begin{array}{c} :\ddot{\text{O}}: \\ \\ \text{H}-\ddot{\text{O}}-\ddot{\text{Cl}}-\ddot{\text{O}}: \\ \\ :\ddot{\text{O}}: \end{array}$	$\left[\begin{array}{c} :\ddot{\text{O}}-\ddot{\text{Cl}}-\ddot{\text{O}}: \\ \\ :\ddot{\text{O}}: \end{array} \right]^-$
Perchloric acid $\begin{array}{c} :\ddot{\text{O}}: \\ \\ \text{H}-\ddot{\text{O}}-\ddot{\text{Cl}}-\ddot{\text{O}}: \\ \\ :\ddot{\text{O}}: \end{array}$	$\left[\begin{array}{c} :\ddot{\text{O}}-\ddot{\text{Cl}}-\ddot{\text{O}}: \\ \\ :\ddot{\text{O}}: \end{array} \right]^-$

Questions

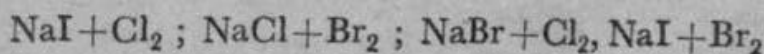
I. Write equations for the following :

- bubbling chlorine through a bromide solution,
- reaction of potassium iodide and ferric chloride,
- heating solid NaBr with H_3PO_4 .

2. From each of the following sets select the substance which best fits the requirement specified.

- (a) strongest acid HOCl , HOClO , HOClO_2 ,
- (b) best reducing agent F^- , Cl^- , Br^- , I^- ,
- (c) best hydrogen bonding HF , HCl , HBr , HI ,
- (d) weakest acid HF , HCl , HBr , HI .

3. (a) Arrange the halogens in order of decreasing ability to function as oxidizing agents.
- (b) The following pairs of substances are mixed in aqueous solution :



Write balanced equations to illustrate any reactions which occur.

4. Explain why the physical properties of hydrogen fluoride, *e.g.* melting point, boiling point, and heat of vaporization are out of line with the trend observed for these properties for the other hydrogen halides.
5. (a) Iodine is much more soluble in a solution of potassium iodide than in pure water. Why?
- (b) Why HF is a relatively weak acid in water solution, whereas the other hydrogen halides are strong acids?
6. Write short notes on :
- (a) oxyacids of the halogens,
 - (b) chemistry of fluorine.
-

CHAPTER 9

THE TRANSITION ELEMENTS

In the Periodic Table, elements are generally classified into A and B Groups. The A Group elements are sometimes called the *main* or *representative* elements, and the B Group elements are called *transition* elements. The transition elements consist of the following four series :

- (1) Sc (21) through Zn (30) ;
- (2) Y (39) through Cd (48) ;
- (3) La (57) through Hg (80) ; and
- (4) Ac (89) through Lw (103).

These series fall into two categories, according to whether they are formed by electrons entering *d* or *f* orbitals. The former are called the *outer transition elements*, or *d block transition elements*, while the latter are called the *inner transition elements* or *block transition elements*. The first two series constitute the outer transition elements, and the remaining two, the inner transition elements. In the first and the second series, electrons fill the *3d* and *4d* orbitals, respectively. The elements immediately following, La, that is Ce (58) to Lu (71), constitute the third transition series called the *lanthanides* (or *rare earths*), and those following Ac, that is, Th (90) to Lw (103), make up the fourth transition metal series, called the *actinides*.

In the lanthanide series the *4f* orbital is being filled and in the actinide series the *5f* orbital. We shall discuss only the first transition series in this chapter.

General Properties : Some of the numerical properties of the first transition series are listed in table 9·1.

1. Electronic Configuration : A *d*-sub shell contains 5 orbitals and hence ten electrons, so that following calcium one finds a block of ten elements, *i.e.* scandium to zinc, in which the *3d* sub-shell is progressively filled up as the atomic number increases. As can be seen from table 9·1, the filling of the inner subshell is not regular. Irregularities in filling are observed at chromium and copper. This is so because it is energetically favoured.

Since the outermost shell of all these elements generally remains constant and the penultimate shell of electrons is expanded, they may be expected to have many physical and chemical properties in common.

Table 9.1
SOME PHYSICAL PROPERTIES OF THE TRANSITION ELEMENTS

Element	Atomic number	Electronic configuration of outer shell	M.P. ($^{\circ}\text{C}$)	BP. ($^{\circ}\text{C}$)	Density (g/cm^3)	Atomic radius (Å)	Electro-negativity	First ionization potential (eV)
Scandium	21	$3d^1 4s^2$	1400	3900	3.1	1.439	1.3	6.5
Titanium	22	$3d^2 4s^2$	1812	3130	4.5	1.324	1.5	6.9
Vanadium	23	$3d^3 4s^2$	1730	3530	6.0	1.224	1.6	6.8
Chromium	24	$3d^5 4s^1$	1900	2480	7.1	1.172	1.6	6.8
Manganese	25	$3d^5 4s^2$	1244	2087	7.2	1.168	1.5	7.4
Iron	26	$3d^6 4s^2$	1535	2800	7.9	1.165	1.8	7.9
Cobalt	27	$3d^7 4s^2$	1493	3520	8.9	1.157	1.8	7.9
Nickel	28	$3d^8 4s^2$	1455	2800	8.9	1.149	1.8	7.6
Copper	29	$3d^{10} 4s^1$	1083	2582	8.9	1.173	1.9	7.7
Zinc	30	$3d^{10} 4s^2$	419	907	7.1	1.249	1.6	9.4

For example, all the transition elements are lustrous metals and are good conductors of heat and electricity.

2. Atomic Size : As the nuclear charge increases with increasing atomic number across the row, it strengthens the electric field attracting the electrons towards the nucleus, thereby decreasing the radius. Hence, the atomic size of the successive elements of the first transition series decreases slightly as their atomic number increases.

3. Density : The densities of the transition elements are high because their atomic volumes are low.

4. Melting and Boiling Points : The melting and boiling points of the first outer transition elements are generally very high. Zinc is a notable exception because the $3d$ sub-shell is completely filled. It may be pointed out that the strength of the bonding between the atoms of metals depends on the interaction between the electrons in their outermost shell. The greater the number of electrons available for interaction, the stronger the resulting bonding. In the alkali metals, which have a single electron in the outermost shell, the interatomic bonding is not strong and, consequently they have relatively low melting points. In the alkaline earth metals, which have two electrons available in the outermost shell, the interatomic bonding is stronger, and consequently, they have higher melting points than the alkali metals. The elements of the first transition series have 3 or more electrons available for bonding, and at least one of these electrons is a d electron. Hence the interatomic bonding is very strong and their melting points are very high.

5. Electropositive Character : Their low electronegativity values indicate that the transition elements are strongly electropositive, and they form stable oxides and halides. These elements show an increasing tendency to remain unreactive. At ordinary temperatures, these metals are unreactive in compact form, but they are quite reactive in finely divided form.

6. Ionization Potentials : The ionization potentials of the transition elements are neither very high nor very low. The values lie intermediate between those for the s - and p -block elements. This suggests that the transition elements are less electropositive than Groups I and II and may form ionic or covalent bonds. The tendency to form ionic bonds decreases as the atomic size increases. It may be

noted that the variation in ionization energy within the series is small; the values lie between 5 and 10 electron volts.

6.5

7. Catalytic Properties : The transition elements and their compounds can be used as effective catalysts because they are able to *adsorb* gases on their surfaces. Examples are iron, (Fe) cobalt, (Co) nickel, (Ni) manganese dioxide (MnO_2) and vanadium pentoxide (V_2O_5).

8. Mechanical Properties : Typical transition metals are generally tough, malleable and ductile.

9. Magnetic Properties : Most of the transition elements are *paramagnetic*, i.e. they are slightly attracted by a magnetic field. Paramagnetism is due to the presence of unpaired electrons. A single or unpaired electron behaves like a small magnet and is attracted by other magnets. Other substances in which all the electrons are paired are not attracted by magnetic lines of force, and are called *diamagnetic*. In pairing, electrons lie pole to pole in such a way that their magnetism is cancelled. Elements such as iron and cobalt, which can be magnetized, are called *ferromagnetic*.

10. Colour : One of the most characteristic features of the transition metals is that they all give coloured ions in aqueous solution and most of their compounds are coloured. Colour is associated with the incompletely filled shells of the ions of these elements and the ability to promote an electron from one energy level to another. In the transition elements, *d* electrons are promoted to a higher energy level within the *d* shell. This corresponds to a fairly small energy difference, and thus light is absorbed in the visible region of the spectrum. It may be noted that a change in colour may be affected by altering the environments of the ion which consequently change the spacing of energy levels.

11. Oxidation States : An extremely important chemical characteristic of the transition elements is that they show *variable valency*, i.e. they are able to exist in a variety of oxidation states in their compounds. This is because of the presence of a partially filled *d*-sub-shell. A wide range of oxidation states is encountered because not only 4*s* but also 3*d* electrons may be involved in bonding. All the elements of the first transition series, except scandium, show an oxidation state of +2 and many show an oxidation state of +3 as well. The common oxidation states are given in table 9.2.

Table 9.2

OXIDATION STATES OF THE TRANSITION ELEMENTS

Elements	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
3d and 4s electrons	3	4	5	6	7	8	9	10	11	12
Common Oxidation States									+1	
		+2	+2	+2	+2	+2	+2	+2	+2	+2
	+3	+3	+3	+3	+3	+3	+3	+3		
		+4	+4		+4					
			+5	+6	+6	+6				
					+7					

It is of interest to know that for the elements from scandium to manganese, the maximum oxidation state correlates with the total number of 3d and 4s electrons. Moreover, the maximum oxidation number increases first regularly from +3 for scandium to +7 for manganese and then decreases to +2 for zinc as one goes across the transition row.

It is worthwhile to remember that there exists a direct relationship between oxidation state, and the basic or acidic character of the oxides formed. For any series of oxides of a transition metal, the basic and also the ionic character diminishes with the increase in oxidation number of the element. This is illustrated below.

Oxidation state of Mn	Oxide	Character
+2	MnO	Basic
+4	MnO ₂	Amphoteric
+7	Mn ₂ O ₇	Acidic

12. Complex Formation : Another outstanding property of the transition elements is their ability to form complex or co-ordination compounds. This is because they have small, highly-charged ions and vacant *d* orbitals for chemical bonding.

This topic will be discussed in the succeeding pages.

13. Interstitial Compounds : These are compounds, in which small, non-metallic atoms (particularly hydrogen, boron, carbon and nitrogen) can penetrate the interstices of the lattice of transition metals, *e.g.*, hydrides, carbides, and nitrides. They are often hard and resistant to hydrolysis. Such compounds are often *non-stoichiometric*, *i.e.*, the atoms are not present in a simple ratio. In other words their composition is variable and may not be expressed by a simple chemical formula. Related to the interstitial compounds are the *alloys*, which consist of two or more different metals.

Complex ions and Co-ordination Compounds: A co-ordination compound contains a metal atom or ion which is surrounded by a number of oppositely charged ions or neutral molecules known as *ligands*. The metal atom is called the *centre atom*, or *centre of co-ordination*. The number of ligands attached to the metal is termed its *co-ordination number*. When the group comprising the metal and its ligands carries a positive or a negative charge, it is called a *complex ion*.

A ligand, also known as *co-ordination group*, may be an ion or a molecule that acts as an *electron-pair donor* in the formation of a covalent bond. It has at least one pair of unshared electrons which is accepted by the vacant orbitals of the metal. If the ligand contains only one donor atom, it is called a *monodentate* or *unidentate*; those having more than one are *multidentate* ligands and are known as *chelating agents*. The compounds containing such complex ions are referred to as *chelates*. If the ligands occupy two, three, four, five or six co-ordinating positions, they are called, *bi—*, *tri—*, *tetra—*, *penta*, or *hexadentate*. For example, ammonia (NH_3) is a *monodentate*, whereas ethylenediamine ($\text{H}_2\text{N} \cdot \text{CH}_2 \cdot \text{CH}_2 \text{NH}_2$) behaves as if there were two molecules of ammonia, and acts as a *bidentate* and a *chelating unit*. The common donor atoms are nitrogen, oxygen and sulphur.

Some of the common ligands are listed in table 9.3.

Table 9.3
COMMON LIGANDS

Ligand	Number of Position
H_2O , NH_3 , OH^- , F^- , Cl^- , Br^- , I^- , CN^- , NO_2^- ,	1
$(\text{H}_2\text{N} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH}_2$ — ethylene diamine)	2
$\text{C}_2\text{O}_4^{--}$ (oxalate), CO_3^{--} , SO_3^{--} CO_3^{2-}	3
$(\text{H}_2\text{N} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH}_2$ — diethylene triamine)	3
$\{(\text{OOC} \cdot \text{H}_2\text{C})_2\text{N} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{N}(\text{CH}_2\text{COO}^-)_2\}$ ethylene diamine tetra acetate.	6

It may be pointed out that most of the properties of co-ordination compounds are governed by the nature of the central metal. Its size and magnitude of its charge, the nature and number of donor atoms and the charge on the ligand.

Nomenclature : (1) The name of the cation is given first, that of the anion last.

(2) The contents of the co-ordination sphere are specified: first the ligands, then the central atom.

(3) The nature of the ligands is indicated by a suffix; positively charged ligands have the suffix-*ium*, neutral ligands have no suffix, and negative ligands have the suffix-*o*. Ammonia, NH_3 , is called *ammine*.

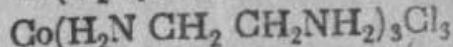
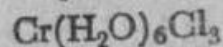
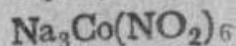
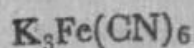
(4) The ligands are named in a definite order depending on their charge : anionic ligands first, then neutral and finally cationic.

(5) The number, *i.e.* two three, four, etc. of each type of ligand is denoted by prefixes, *di—*, *tri—*, *tetra—*, and so on. In order to indicate the number of complete groups of atoms, *e.g.*, the number of organic ligands attached to a metal atom, the prefixes *bis—*, *tris—*, *tetrakis—*, etc., are used.

(6) The oxidation number of the metal is indicated by a Roman number in parentheses immediately following its name. An anionic

complex is denoted by the suffix *-ate*, whereas cationic or neutral complexes have no suffix.

Examples



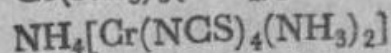
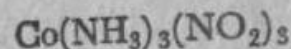
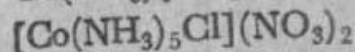
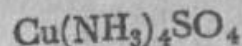
potassium hexacyanoferrate (III)

sodium hexanitrocobaltate (III)

hexa aqua chromium chloride (III)

tris (ethylenediamine) cobalt (III) chloride.

Examples



tetra ammine copper (II) sulphate
chloropentammine cobalt (III)
nitrate.

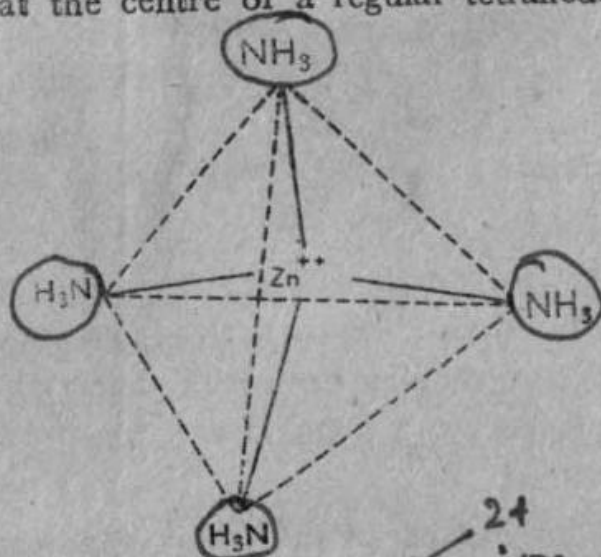
trinitro triammine cobalt (III).

ammonium tetrathiocyanato-
diamminechromate (III).

Geometry of Complexes : The geometrical structures of a complex ion are determined by the co-ordination number (C.N.) of the central atom. Co-ordination numbers range from 2 to 8, the most common being 4 and 6. We shall now discuss the structures of important types of complexes in relation to the co-ordination number involved.

Co-ordination Number Four : A metal complex having four ligands in its co-ordination sphere shows two geometric arrangements (1) the tetrahedral, and (2) the square planar.

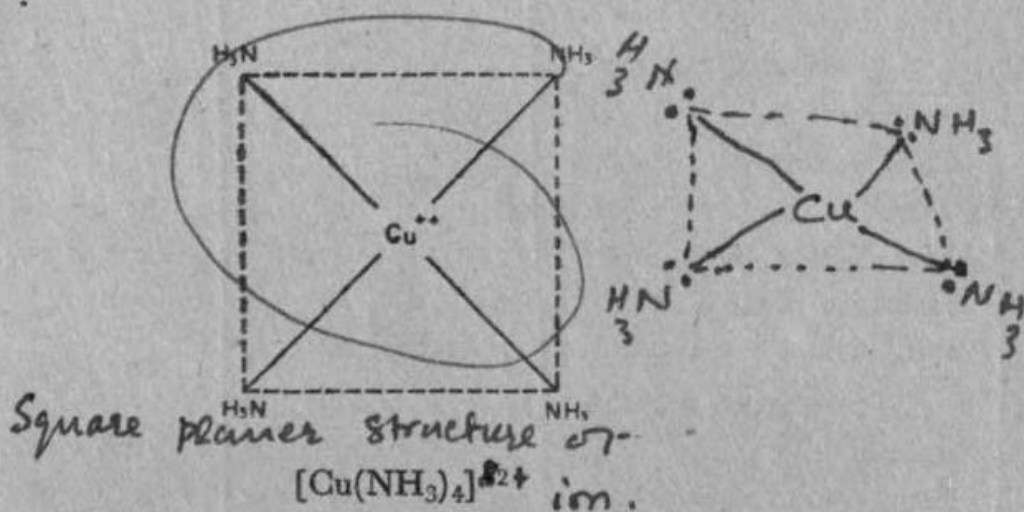
Tetrahedral Structure : In the tetrahedral arrangement, the central atom is at the centre of a regular tetrahedron, and the four



Structure of $[\text{Zn}(\text{NH}_3)_4]^{2+}$ ion.

co-ordinating groups occupy the corners of the tetrahedron. Such a complex involves hybridization of one s and three p orbitals, forming a set of four equivalent sp^3 hybrid orbitals with lobes tetrahedrally directed in space. Nickel (0), copper (I) and zinc (II) form tetrahedral complexes because they have only $4s$ and $4p$ orbitals available; the $3d$ orbitals are completely occupied by unshared pairs. Examples of tetrahedral complexes are $\text{Ni}(\text{CO})_4$, $\text{Cu}(\text{CN})_4^{-3}$, and $\text{Zn}(\text{NH}_3)_4^{+2}$.

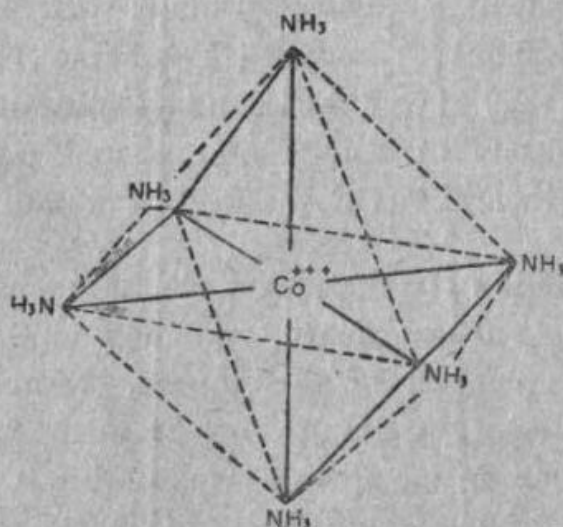
Planar Structure : In the square planar arrangement the central atom is at the centre of the square, and the four donor atoms of the ligands occupy the corners of the square. Moreover, the central atom and the four co-ordinating groups lie in the same plane. Such complexes utilize one d , one s , and two p orbitals for hybridization giving rise to a set of four equivalent dsp^2 hybrid orbitals with lobes directed to the corners of a square in the xy plane. In the first transition series, the square planar arrangements are common for $\text{Ni}(\text{II})$ and $\text{Cu}(\text{II})$. Examples of planar complexes are $\text{Ni}(\text{CN})_4^{-2}$, CuCl_4^{-2} and $\text{Cu}(\text{NH}_3)_4^{+2}$.



Co-ordination Number Six : Complex compounds exhibiting a co-ordination of six are the most numerous of all. They are found in only one geometrical arrangement, the octahedron.

Octahedral Structure : In the octahedral arrangement the central atom is at the centre of an octahedron and the ligands are at the six corners. When two d , one s and three p orbitals on a given atom are hybridized, a set of six equivalent d^2sp^3 bonding orbitals with lobes directed towards the apices of an octahedron can be formed. The hybrid orbitals are occupied by six pairs of electrons supplied by donor

atoms of the ligands. Examples of octahedral complexes are $\text{Co}(\text{NH}_3)_6^{3+}$, $\text{Fe}(\text{CN})_6^{3-}$, FeF_6^{3-} , $\text{Co}(\text{NO}_2)_6^{3-}$ and $\text{Cr}(\text{H}_2\text{O})_6^{3+}$.



The structure of the $[\text{Co}(\text{NH}_3)_6]^{3+}$ ion

Octahedral co-ordination occurs very extensively among the elements of the first short transition series especially with Fe (II), Fe (III), Mn (II), Cr (III) and Co (III).

Uses of Complex ions : The complex ions find application in analytical chemistry as precipitating agents and separational agents. They assume an important role in biological processes. Chlorophyll, haem (a component of blood haemoglobin) and vitamin B₁₂ contain Mg (II), Fe (III) and Co (III) respectively. The exact role of these metals in plant and animal life is not yet fully understood. The metal complexes are also used as aids in dyeing.

Scandium : Scandium is a rare element. It shows an oxidation state of only +3. In contrast to other members of the series scandium forms colourless compounds. It reacts with water to liberate hydrogen. Scandium resembles aluminium in many respects.

Titanium : The chief ores of titanium are *rutile*, TiO_2 ; and *elementite*, FeTiO_3 . It is very difficult to prepare titanium in the pure state because it reacts readily with oxygen, carbon, nitrogen and hydrogen at high temperatures. Even small quantities of impurities render the metal brittle and useless. However, pure titanium metal may be obtained by reducing TiCl_4 with magnesium at 300°C in an atmosphere of argon :



Because of its high melting point and resistance to corrosion, it is used in the construction of aeroplanes and jet engines.

Vanadium : Vanadium resembles titanium in its physical and chemical properties. Because of its high reactivity, it is difficult to obtain pure. The metal is extensively used in the manufacture of special steels. Addition of a small quantity of vanadium to steel increases the tensile strength, toughness and resistance to shock and vibration. Thus vanadium alloy steels are used in the production of high-speed tools and heavy machinery. Vanadium pentoxide, V_2O_5 , an orange powder, is used as a catalyst in the contact process for the manufacture of sulphuric acid. The compounds of vanadium are well known for their varied colours. For instance, the V^{++} ion has a deep violet colour, the V^{+++} ion is green, the vanadyl ion, VO^{++} , is blue, VO_2 is a dark green substance, the VO^{3+} ion is yellow, V_2O_5 is orange, and VO_4^- is red.

Chromium : The principal ore of chromium is *chromite*. The formula of this ore may be written as either $FeCr_2O_4$, $FeO \cdot Cr_2O_3$, or $Fe(CrO_2)_2$. The metal may be obtained by the reduction of chromium trioxide, Cr_2O_3 , with aluminium, by means of a method called *Goldschmidt's aluminothermic process or thermite process*.

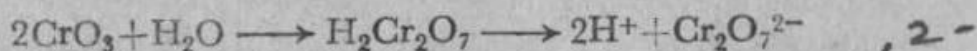


The reaction is highly exothermic. When dipped in nitric acid, the metal becomes "passive" i.e., it is rendered chemically inactive due to the formation of an oxide coating. Because of its brilliant lustre and resistance to corrosion, chromium is widely used as a plating material. It is extensively employed in the manufacture of alloy steels which are very hard, tough and resistant to corrosion. The chrome steels are used in the manufacture of armour plates, projectiles and safes. *Stainless steel* is an alloy of about 64 percent iron, 18 percent chromium and 8 percent nickel. *Nichrome*, which contains about 60% nickel, 15% iron, and 15% chromium, is used in the form of wire for electric heating elements because of its high electrical resistance, melting point and resistance to corrosion.

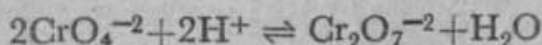
Chromium exhibits oxidation states of +2, +3 and +6. The compounds in which the metal shows an oxidation number of +3 are the most stable, and those with the +6 number are quite stable. The compounds with chromium in the +2 oxidation state are very unstable, and thus act as powerful reductants. It may be of interest to note that all compounds of chromium in these oxidation states are highly coloured. The chromous ion (Cr^{2+}) has a beautiful blue colour.

The black chromous oxide, (CrO) is basic ; the green chromic oxide (Cr₂O₃) is amphoteric, and the dark red chromic anhydride (CrO₃) is acidic.

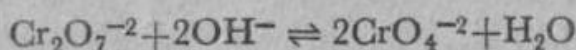
The chromic anhydride, in which chromium shows its highest oxidation state of +6, dissolves readily in water to form a strongly acid solution :



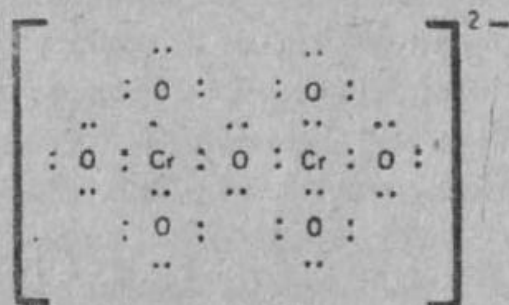
Dichromic acid, H₂Cr₂O₇, exists only in solution. Its salts are called *dichromates* and contain the dichromate ion (Cr₂O₇²⁻). Another acid which contains chromium in the +6 oxidation state is the chromic acid (H₂CrO₄). This acid, too, exists only in solution. Its salts, which are called *chromates*, contain the chromate ion, (CrO₄²⁻). On addition of an acid, the yellow chromate ion is converted to the orange-red dichromate ion :



The process can be reversed by the addition of a base :

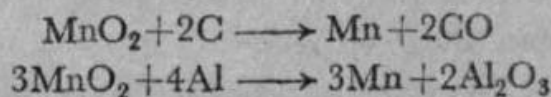


The chromate ion has a tetrahedral structure. In the dichromate ion, there are two tetrahedrons linked together through a common oxygen atom. The electronic structure of Cr₂O₇²⁻ is shown below :



Both chromate and dichromates are strong oxidizing agents, the chromium being reduced from +6 to +3 state in acid solution. The insoluble chromates such as PbCrO₄ and BaCrO₄ are used as paint pigments. A mixture of K₂Cr₂O₇ and concentrated H₂SO₄ is used in cleaning laboratory glassware. Sodium dichromate (Na₂Cr₂O₇ · 2H₂O) is largely used in the tanning of hides, to produce "chrome-tanned" leather.

Manganese : The principal ore of manganese is *pyrolusite*, MnO₂. Impure manganese may be obtained by reducing MnO₂ with carbon or aluminium :



The reactions become smoother if Mn_3O_4 is used which is easily obtained from MnO_2 simply by heating. The metal is mostly used in the manufacture of alloy steels. Two most common alloys of iron and manganese are *spiegeleisen* (15-20% Mn) and *ferromanganese* (75-80% Mn). When added in small amounts, manganese improves the quality of steel by removing sulphur and oxygen as MnS and MnO_2 .

Manganese dioxide in which the metal exhibits the +4 oxidation state is a well-known compound. It acts both as an oxidizing agent (Mn^{4+} to Mn^{2+}) and a reducing agent (Mn^{4+} to Mn^{7+}). It is used for decolourizing glass and in dry cells.

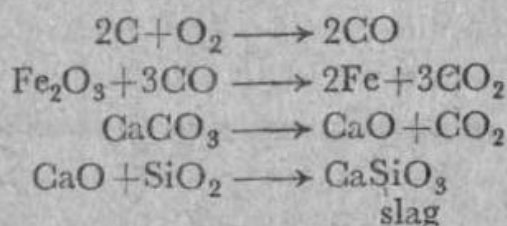
The most important compound of manganese is potassium permanganate, KMnO_4 , which contains manganese in the +7 oxidation state. The salt has a deep purple-red colour and dissolves readily in water. It is a powerful oxidizing agent and is widely used in analytical chemistry. Generally, the MnO_4^- ion is reduced to the Mn^{++} ion in acid solutions, but to MnO_2 in basic solutions. It is of interest to note that the MnO_4^- ion is purple while the Mn^{++} ion is colourless. Potassium permanganate is also used as a disinfectant.

Iron : Iron is by far the most important and useful of all the metals in every day use. Pure iron has little use because it is too soft and weak. The addition of small amounts of alloying elements such as carbon and other transition elements improves the properties of the metal which finds applications in a variety of ways. The main products of iron are cast iron, wrought iron, and steel.

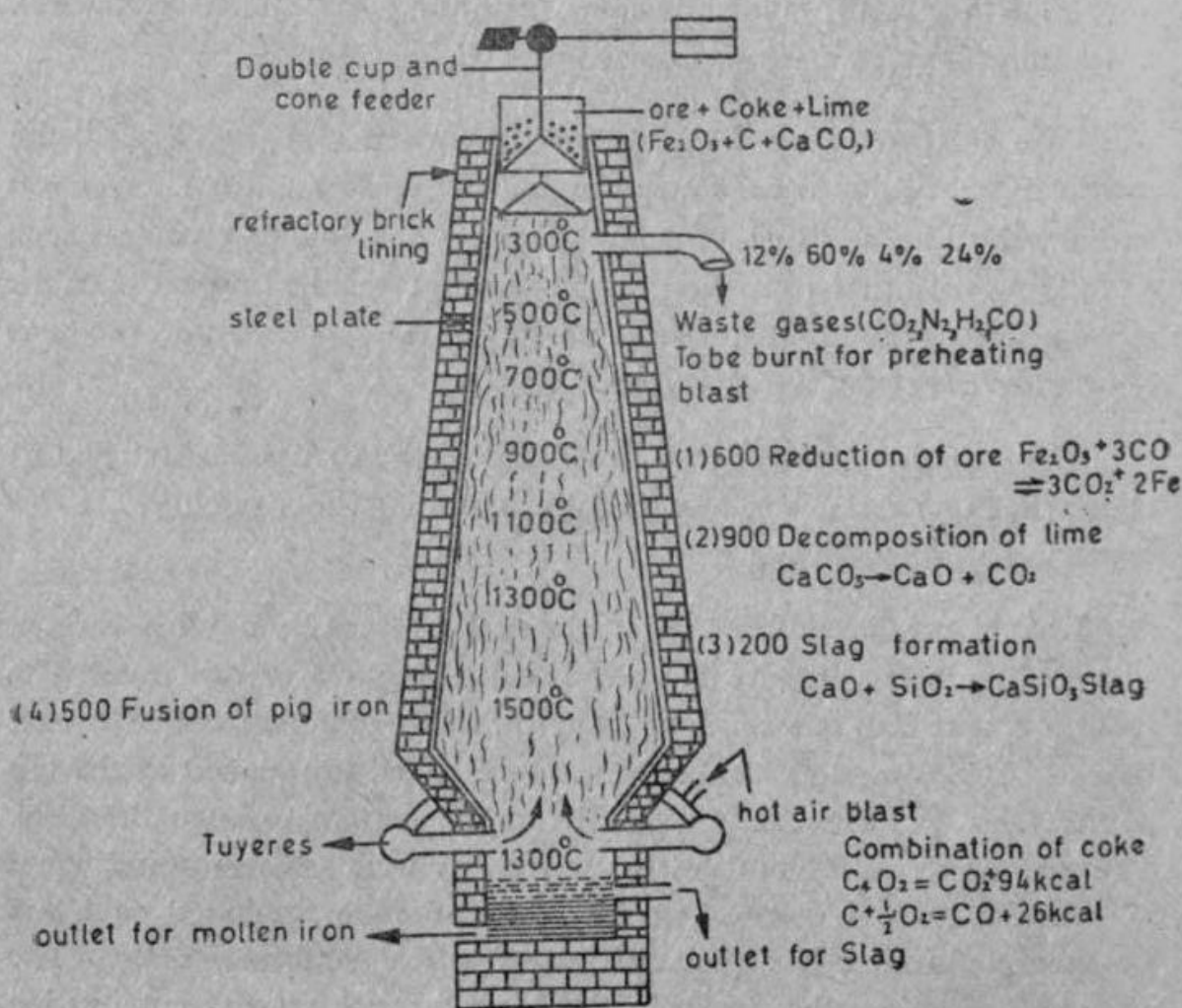
The principal ores of iron are *haematite* (Fe_2O_3) *magnetite* (Fe_3O_4) *siderite* (FeCO_3) and *iron pyrites*, (FeS_2) often called "fool's gold". It also occurs free in meteorites.

Iron is produced from its oxide ores by reduction with carbon. The product is very impure iron and is called *pig iron* or *cast iron*. The process is carried out in a huge cylindrical structure called a *blast furnace*. Ore, limestone and coke are mixed and introduced at the top of the furnace. Hot air is blown in at the bottom to burn the coke. The coke serves as a fuel to melt the iron as well as a reducing agent to convert the oxide ore to metal. Limestone is employed as a flux for ores containing large quantities of silica to form a *slag*. The important reactions that occur in the blast furnace are the combustion of coke to carbon monoxide, the reduction of the oxide ore with CO , the

decomposition of limestone into CaO , and the combination of CaO (basic oxide) and SiO_2 (acid oxide) to form slag :



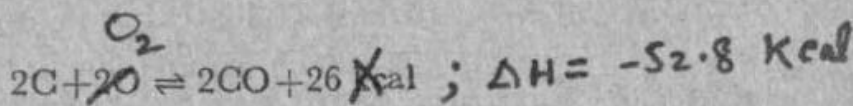
The molten iron and slag are collected in the *crucible* at the bottom of the furnace. The slag floats on the surface of the melt and is drawn off. The product which is tapped from the blast furnace is called *pig iron*, which is impure, containing about 4% carbon and small quantities of silicon, sulphur, phosphorus, manganese and other impurities. Because of its hardness and brittleness, pig iron cannot be used for structural purposes. However, it is useful for manufacturing objects which are not subjected to high strains or violent shocks. It is treated further to produce steel and alloys. A diagram of the blast furnace and its more detailed description is given below:



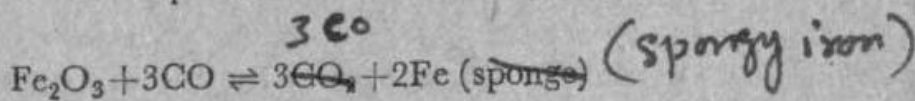
The blast Furnace

The Blast Furnace : A cylindrical furnace 80-100 feet high and constructed of steel plates lined with refractory bricks. The mouth of the furnace is closed by a cup-and-cone device. The materials for charging the furnace are tipped into the cup of the feeder. When the cup is filled, the cone is depressed, and the charge is automatically distributed into the interior of the furnace. Waste gases pass away from the outlet at the top of the furnace. For the molten slag and the molten iron two taps are provided at the base of the furnace.

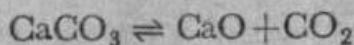
The mixture of roasted (calcinated) ore, coke and lime stone is fed into the top of the furnace. A blast of preheated air is forced into the base of the furnace through water cooled nozzles called *tuyeres*. The first chemical reaction taking place in the furnace is the burning of coke to carbon monoxide which raises the temperature to 1500°C at the base of the furnace.



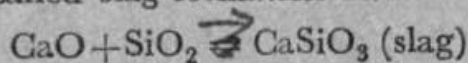
Now the stream of solid material is coming downwards while a hot current of carbon monoxide is moving upwards. The two meet at the *reduction zone* at a temperature of 600°C when spongy iron is obtained.



The limestone in the charge is decomposed to calcium oxide and carbon dioxide at 900°C in the lime decomposition zone; sulphur in the fuel is absorbed by the iron.



At 1200°C phosphates in the ore are reduced to phosphorus and silica to silicon, phosphorus and silicon both alloy with the iron like sulphur. The remainder of the silica (SiO_2) in the charge combines with CaO to form a fusible material, *slag*, which floats on molten iron and can be removed. This is called slag formation zone.

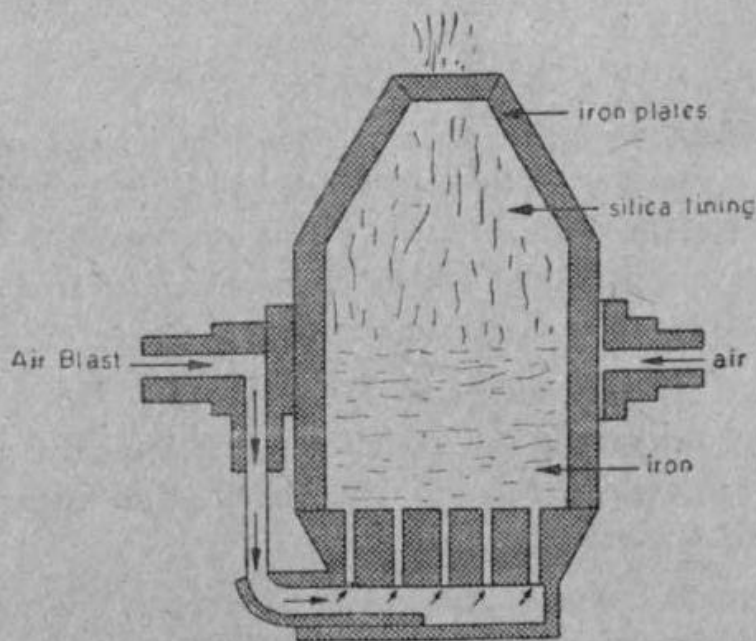


At 1500°C the spongy iron containing P, S, Si and C melts. The fused iron is run out of the hearth from time to time into sand moulds where it solidifies as pig-iron.

Steel is made from pig iron. There are three principal processes for the conversion of pig iron to steel : (1) the open-hearth process, (2) the Bessemer process, and (3) the electric process. These methods involve the reduction of the carbon content of pig iron to between 0.1 and 1.5% and the sulphur and phosphorus to 0.05% or less. Sulphur

and phosphorus are highly objectionable in steel because they make it brittle. The open-hearth process produces a higher-quality steel than the Bessemer process, though it is relatively slow. In this process careful control of the product is possible because analyses are made during the run. It also produces more steel at each operation. Fuel costs are high. The Bessemer steel is cheaper, but the steel is not so good as open-hearth steel. The process is so rapid that its careful control is not possible. The electric process is employed for making special high-quality hard steels. This process allows an accurate control of temperature and other conditions. *Mild steel* or *low-carbon steels* contain less than 0.2% carbon. They are soft, malleable and ductile. They are used in making boiler plates, bars, rivets, bolts and nuts. *Medium steels* contain 0.2 to 0.6% carbon and are employed for making rails, axles, beams and girders. Unlike cast iron, mild steels and medium steels can be forged (shaped by hammering and pressing while hot) and welded. *High-carbon steels*, containing 0.75 to 1.50% carbon, are used for making engines, surgical instruments, razors, drills and other tools. A more detailed description of the Bessemer converter and the open hearth process is given below.

The Bessemer Converter : In this process about ten tons of molten pig-iron are run into a large pear-shaped iron vessel, lined inside with silica bricks and provided with holes at the bottom through

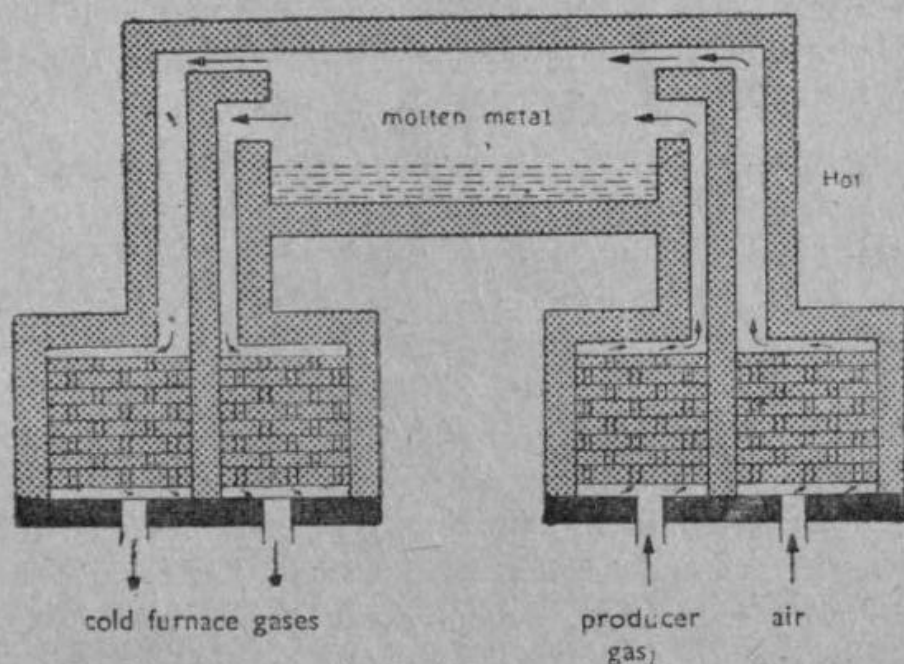


The Bessemer Converter

which a powerful air blast can be blown. It is supported on a central axis, and can be tilted down. The converter is tilted and charged.

The blast is turned on, the temperature rises due to the heat evolved by the oxidation and combustion of the impurities, silicon manganese and carbon. The carbon forms CO which burns at the mouth of the converter. The other oxides form a slag with the lining. The blast is stopped as soon as the blue flame vanishes. The converter is again tilted and a calculated amount of spiegeleisen (an alloy of Fe with 6-12% Mn and 5% C) is added and the blast turned on again for a few minutes. The molten metal is then cast into moulds. When the impurity is phosphorus, the converter is lined with a basic material, a mixture of magnesia and lime. The phosphorus forms $\text{Ca}_3(\text{PO}_4)_2$ and is removed as slag. The converter lined with silica is called acid Bessemer and that with lime lining a basic Bessemer.

The Open-hearth Process : In this process the furnace is charged with a mixture of pig-iron, scrap iron and good haematite ore free from carbon. The mixture is melted in a shallow rectangular hearth lined with silica or dolomite and heated by producer gas. Both the gas and the secondary air for the combustion of the gas are preheated so that a very high temperature can be obtained. The carbon is oxidised away until the required proportion is left. Manganese is added as ferromanganese to remove sulphur by forming manganous



The Open-hearth Process

sulphide and to decompose ferric oxide, and the liquid steel is poured into moulds to solidify.

Wrought iron is almost pure iron with only less than 0.1% carbon. It is made by melting pig iron with Fe_2O_3 which oxidises the impurities. Wrought iron is very tough and strong and can be readily forged and welded. It resists corrosion better than steel. It is used for making chains, horse shoes and similar objects.

Rusting : The corrosion of iron is called *rusting*. The process occurs only in the presence of (1) oxygen, (2) water, and (3) carbon dioxide or some other compound, acid or salt, which forms the electrolyte in aqueous solution. Rusting is an electrochemical process which involves the transfer of electrons along the surface of the metal under the influence of a potential difference. The end-product of the process, rust, appears to be a hydrated ferric oxide ($\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$).

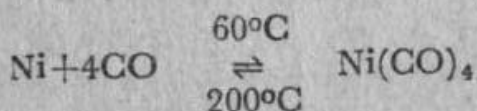
Rusting may be prevented by keeping air and moisture away from the metal. This may be achieved by a protective coating of paint, grease, or some other metal such as zinc (galvanizing), tin, chromium and nickel. Corrosion is also inhibited by lowering the reactivity of metal by alloying as in stainless steel.

Cobalt : Cobalt always occurs in combination with nickel. The most important ores of cobalt are *smaltite*, CoAs_2 , and *cobaltite*, CoAsS . The metal is tougher, stronger and harder than pure iron. It is slightly ferromagnetic. Cobalt is extensively used for making permanent magnets. It is also used in the manufacture of alloy steels for making high-speed cutting tools and surgical instruments.

Like iron, cobalt exhibits oxidation states of +2 and +3. The divalent compounds are more stable and more important than the trivalent. Unlike ferrous ion, the cobaltous ion $\text{Co}(\text{H}_2\text{O})_6^{2+}$ is quite stable and is not easily oxidised to cobaltic ion. Cobalt salts; in hydrated form or in solution; are generally pink or blue. A dilute solution of cobaltous chloride, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, is light pink in colour and is used as an 'invisible' ink. On warming, the colour changes from pink to blue because of the dehydration of the salt. The hydrated Co^{3+} ion is a very powerful oxidizing agent. It can even oxidize water, liberating oxygen and forming cobaltous ion. The complexes of cobalt +3 are very stable, e.g., sodium cobaltinitrite, $\text{Na}_3\text{Co}(\text{NO}_2)_6$. The last-named complex is used as a test for K^+ ions.

Nickel : A common ore of nickel is *millerite*, NiS . The metal is prepared by *roasting* (heating in air) nickel sulphide to form nickel oxide. The oxide is reduced with carbon to the nickel metal. High

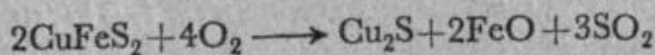
purity nickel may be produced by passing carbon monoxide over the metal at 60°C and thermally decomposing the nickel carbonyl, $\text{Ni}(\text{CO})_4$ at 200°C :



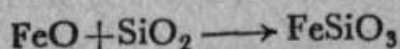
Nickel is very similar to cobalt in physical and chemical properties. It is less ferromagnetic than iron. Nickel metal is used mostly in making ferrous and non-ferrous alloys. Among the ferrous alloys, we have already mentioned *stainless steel* and *nichrome*. Non-ferrous alloys include : *monel metal* (70% Ni, 30% Cu), widely used in chemical industry ; and *cupro-nickel*, (75% Cu, 25% Ni) used in coinage. Pure nickel is used in electroplating. Finely-divided nickel, which is highly reactive is an outstanding catalyst and is largely used in the hydrogenation of vegetable oils to *Banaspati Ghee*.

The most important oxidation state of nickel is +2. In aqueous solution nickel (II) exists as the green hexaaquo ion, $\text{Ni}(\text{NH}_3)_6^{2+}$, and salts of nickel (II) are generally green. Nickel sulphide, NiS is black as is cobalt sulphide, CoS . Nickel (II) forms octahedral complexes such as $\text{Ni}(\text{NH}_3)_6^{2+}$ which are paramagnetic with two unpaired electrons. These complexes are green or violet. It also forms square planar complexes, e.g., $\text{Ni}(\text{CN})_4^{2-}$, which are diamagnetic and coloured yellow or red.

Copper : Copper is found in the free state, and in the combined as oxides, sulphides and carbonates. The most important ore of this metal is *chalcocite*, Cu_2S . Most of the copper is obtained from the sulphide ore. The ore is *roasted* at red heat in the presence of an excess of air and is converted to copper sulphide and sulphur dioxide :

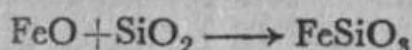
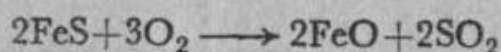
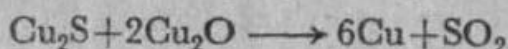
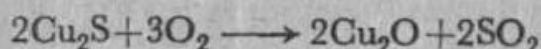


The ferrous oxide produced during the roasting is removed by heating the roasted ore with sand (SiO_2). Ferrous silicate, FeSiO_3 , is formed as a slag which floats on the top of a molten layer of a mixture of cuprous sulphide and ferrous sulphide, called *matt* :

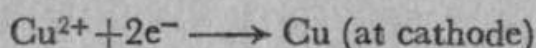
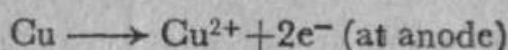


The molten metal, mixed with sand, is run into a converter and

air is blown through the mixture. The following reactions occur :



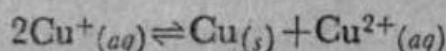
Copper is obtained as a molten metal. As it solidifies, sulphur dioxide escapes forming blisters on the surface of the metal. *Blister copper* is 99% pure, which is generally further refined by an electrolytic process. Blocks of blister copper serve as anodes and plates of pure copper as cathodes. The electrolyte is an aqueous solution of copper sulphate, sulphuric acid, and sodium chloride. Voltage across the cell is carefully controlled so that only copper, which dissolve from the anode, is deposited on the pure copper plates. Metals less electropositive than copper (*e.g.*, Ag and Au) are unaffected and drop from the anode in the form of a sludge called *anode mud*. The following reactions occur at the electrodes :



The *electrolytic copper* is 99.99% pure.

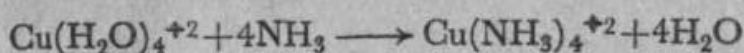
Copper is extremely malleable and ductile and has high thermal and electrical conductivity. It is second only to silver as a conductor of electricity. The metal is extensively used in electrical circuits and appliances. It is also used widely in the constructions of steam pipes and boilers. Large amounts of copper are used in the preparation of alloys such as the *brasses* (Cu + Zn) and *bronzes* (Cu + Sn).

Copper forms two series of compounds: (1) *cuprous* in which copper shows an oxidation state of +1, and (2) *cupric*, in which copper exhibits +2 oxidation state. The cupric compounds are more stable and are thus more commonly used. The cuprous ion, $\text{Cu}(\text{H}_2\text{O})^+$, in aqueous solution is very unstable, and the cuprous compounds except the very insoluble ones, are easily oxidized. This ion has a great tendency to undergo *disproportionation*, *i.e.*, mutual oxidation and reduction into copper and cupric ion :



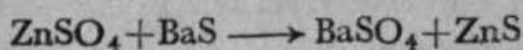
The equilibrium constant $K = [\text{Cu}^{2+}]/[\text{Cu}^+]^2 = 1.6 \times 10^6$ liters/mole at 25°C for the reaction shows that the equilibrium lies far to the right-hand side. This indicates that Cu^+ is a stronger reducing agent than Cu .

The most important cupric salt is copper sulphate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, which forms blue crystals. Copper sulphate is used in electroplating and dyeing. It is also used as a fungicide, to prevent the growth of fungi and algae in swimming pools and reservoirs. On heating, copper sulphate loses its water of crystallization to form the white anhydrous salt. The anhydrous salt is often employed to test for the presence of water in organic liquids. On hydration, it turns blue. The hydrated cupric ion, $\text{Cu}(\text{H}_2\text{O})_4^{+2}$, which occurs in aqueous solutions and in some of the hydrated crystals, has a light-blue colour. The cupric salts are generally blue or green. Cupric sulphide, CuS , is black. When treated with an excess of aqueous ammonia, the copper (II) ion forms an ammoniated complex :



The tetraamminecopper (II) ion, $\text{Cu}(\text{NH}_3)_4^{+2}$ is deep blue and is paramagnetic due to an unpaired electron. The complex has a planar structure, with copper atom at the centre of a square and the four ammonia molecules occupying the corners. This ion is only slightly dissociated and is often used as a test for cupric ion.

Zinc : The principal ore of zinc is *zinc blende*, ZnS . Zinc may be obtained by the usual process of *roasting* the sulphide ore to the oxide. The roasted oxide is then reduced to the metal by heating with coke. We have already mentioned that zinc is used in making *galvanized* iron and *brasses* and *bronzes*. The metal is also used as the container for "dry" batteries and serves as the cathode in dry and wet cells. Zinc shows an oxidation state of only +2. Since all the five 3d orbitals are completely filled, the zinc ion, Zn^{+2} is colourless and not paramagnetic. Pure zinc sulphide is an important compound which finds extensive use in the preparation of a white paint called *lithopone*—an equimolar mixture of zinc sulphate and barium sulphide :



It is also used in making fluorescent paints for coating screens of cathode-ray tubes and television sets.

Questions

1. Complete and balance :
 - (a) $\text{Cr}_2\text{O}_3 + \text{Al} \longrightarrow$
 - (b) $\text{MnO}_3 + \text{H}_2\text{O} \longrightarrow$
 - (c) $\text{CrO}_4^{-2} + \text{H}^+ \longrightarrow$
 - (d) $\text{MnO}_2 + \text{HCl} \longrightarrow$
 - (e) $\text{Co}(\text{NO}_2)_3 + \text{NO}_2^- \longrightarrow$
 - (f) $\text{Cu}^{+2} + \text{NH}_3 \longrightarrow$
2. Compare the elements of the first transition series in regard to (a) atomic radii, (b) melting points, (c) electropositive character, (d) ionisation potentials, and (e) colour.
3. Name the following compounds and give the oxidation number of chromium or manganese in each :
 CrCl_3 , H_2CrO_4 , $\text{Cr}_2(\text{SO}_4)_3$, MnO_2 , MnS , KMnO_4 , Na_2MnO_4 .
4. Using *s*, *p*, *d*, *f* notation, write electronic configurations of the following elements :

Cu, Fe, Ni, Cr and Zn.
5. Name the following complexes :
 $\text{K}_4[\text{Fe}(\text{CN})_6]$; $\text{Na}_3[\text{Co}(\text{NO}_2)_6]$; $[\text{Cr}(\text{NH}_3)_3\text{Cl}_3]$;
 $[\text{Co}(\text{H}_2\text{O})_6]\text{SO}_4$; $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$.
6. Which of the following species are likely to be paramagnetic?
 - (a) $[\text{Fe}(\text{CN})_6]^{4-}$;
 - (b) $[\text{Fe}(\text{CN})_6]^{3-}$;
 - (c) $[\text{Cr}(\text{NH}_3)_6]^{3+}$;
 - (d) $[\text{Co}(\text{NH}_3)_6]^{3+}$.
7. Water and ammonia molecules act as ligands, but H_3O^+ and NH_4^+ do not. Explain.
8. Explain why vanadium metal is difficult to obtain in the pure state ?
9. List the names and formulas of important ores of iron. Give raw materials and functions of each for the manufacture of pig iron in the blast furnace. Write equations for reactions occurring in the furnace.
10. Name six elements which can be alloyed with iron. Also give names and uses of the alloys so formed.

11. Give conditions favouring the rusting of iron. How can corrosion be prevented?
 12. Outline the principal steps involved in the production of electrolytic copper from its sulphide ore. Give equations for chemical reactions involved in the process.
 13. Explain the changes that occur when (a) a copper sulphate crystal is heated; (b) aqueous ammonia is added to copper sulphate solution.
 14. Draw probable structures for each of the following :
(a) Ni(CO)_4 ; (b) $[\text{Ni(CN)}_4]^{2-}$; (c) $[\text{Ni(NH}_3)_6]^{2+}$.
-

CHAPTER 10

NOBLE GASES

Helium, neon, argon, krypton, xenon and radon are placed in the group VIII of the periodic table, because they contain eight electrons, except helium, in their outermost orbit. In some books this group is treated under the heading of zero group elements because of their long reputed inertness.

The first inert gas was isolated in 1895 by Ramsay and Rayleigh. This gas was called argon (which means inert) and it occurs in the atmosphere to the extent of 0.93%. Neon (new), krypton (hidden), xenon (stranger), and radon (radioactive emanation) were isolated at about the end of the nineteenth century.

Some of the important physical properties of these gases along with their electronic configurations are given in the table below (10.1).

Table 10.1

PHYSICAL PROPERTIES OF NOBLE GASES AND THEIR ELECTRONIC CONFIGURATIONS

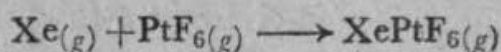
Atomic number	Electron configuration	Ionization potential (kcal/mole)	B.P. °C	ΔH_{vap} (kcal/mole)
He 2	1s ²	567	-269	0.022
Ne 10	2s ² 2p ⁶	497	-246	0.44
Ar 18	3s ² 3p ⁶	363	-186	1.50
Kr 36	4s ² 4p ⁶	323	-153	2.31
Xe 54	5s ² 5p ⁶	280	-107	3.27
Rn 86	6s ² 6p ⁶	247	- 65	4.30

The above table shows that these gases have complete *s* and *p* subshells. Because of this they are inert and only show weak interactions (Van der Waal's interactions) between the individual atoms and thus exhibit extremely low heats of vaporization and boiling points.

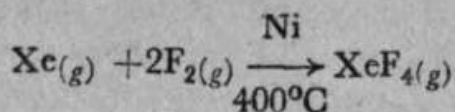
Their ionization potentials are much higher than the ionization potentials of alkali metals (90—124 kcal/mole). In the past, all the attempts to prepare any chemical compounds from them were unsuccessful. This inertness yielded to the concept of 'the stable octet'. As a matter of fact the octet rule formed the basis of first electronic bonding theory during 1916. However there are reasons to believe that these inert gases should yield some chemical compounds. If we compare the ionization potential of xenon (280 kcal/mole) with the ionization potential of hydrogen (313), nitrogen (335), oxygen (314), fluorine (402), and chlorine (300), we find that the ionization potential of xenon is lower than the ionization potentials of hydrogen, nitrogen, oxygen, fluorine and chlorine, all of which form chemical compounds. One further reason for the speculation that the noble gases might react is the idea of the formation of co-ordination complexes by donating electron pairs. After all, noble gases are rich in lone pairs and their ionization potentials are not very different from those of ammonia, water and ethylene.

THE INERT GASES BECOME REACTIVE

In June 1962, N. Bartlett claimed that xenon reacted with gaseous platinum hexafluoride at room temperature to yield an orange yellow solid.



The product known as xenon hexafluoroplatinate was the first noble gas compound made in the laboratory. This caused a stir in the chemical world and regular work on the noble gas chemistry was started at the Argonne National Laboratory in Chicago. After a few months a report from the Argonne Laboratory claimed that xenon reacted directly with fluorine when the two gases were heated under pressure in a nickel container at 400°C.



Now it is known that xenon gives three fluorides namely, XeF_2 , XeF_4 , and XeF_6 . Some of the properties of these fluorides are given in the table 10.2 and their methods of preparation and structure are discussed in the following pages.

Table 10.2**PROPERTIES OF THE FLUORIDES OF XENON**

Property		XeF_2	XeF_4	XeF_6
Melting point ($^{\circ}\text{C}$)	..	140	114	46
Density (g/ml)	..	4.32	4.04	..
Solubility in liquid HF at 25°C (g/100 g)	..	175	4	250
Heat of solution (kcal/mole)	..	2.5	6.7	18
Vap. pressure (mm Hg at 25°)	..	3	4	30
Heat of sublimation (kcal/mole)	..	12.3	15.3	9.0
Bond length XeF(A)	..	2.0	1.95	1.91

COMPOUNDS OF NOBLE GASES

Fluorides : Xenon difluoride is prepared by irradiating xenon and excess of fluorine with mercury arc light for one day at 25°C at $\frac{1}{2}$ atmospheric pressure. The product is a white crystalline solid which should be cooled to -78°C as it is formed. If the cooling is not done, some xenon tetrafluoride is also formed, and these two compounds are not easy to separate. The melting point of xenon difluoride is 140°C which is much higher than xenon (-111°C) and fluorine (-223°C). The density of xenon difluoride is greater than solid xenon (3.1) or fluorine (1.3). Xenon difluoride dissolves readily in anhydrous hydrogen fluoride giving a non-conducting solution. Xenon difluoride is diamagnetic, which means that it does not contain any unpaired electron in its structure.

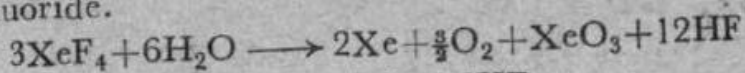
Xenon tetrafluoride is prepared by subjecting xenon and fluorine to 13 atmospheric pressure and 400°C in a nickel container for one hour. Under reduced pressure the compound sublimes readily and beautiful colourless crystals may be thus obtained. The properties of xenon tetrafluoride are also given in table 10.2.

The melting point and density of the tetrafluoride are much lower than the difluoride. The heat of vaporization is 25% higher. The crystals are monoclinic and the molecule is believed to be square planar with a bond angle of 90° . Xenon and fluorine bond distance in the tetrafluoride is slightly less than that of the difluoride. When xenon is heated with large excess of fluorine at 200 atmospheric pressure and 250°C , xenon hexafluoride is obtained. This compound is less stable than the difluoride and tetrafluoride.

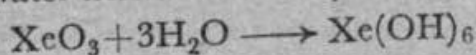
The properties of hexafluoride are also listed in table 10.2. This compound has higher solubility in hydrogen fluoride and unlike the solutions of the difluoride and tetrafluoride this solution is a good conductor of electricity. When heated to 240°C the colourless crystals of hexafluoride turn to pale yellow and finally give a yellow liquid. The structure of hexafluoride is octahedral. It is not conclusively known whether all the bond lengths are equal.

Oxides and Oxyfluorides: Xenon also forms xenon trioxide (XeO_3), xenon tetraoxide (XeO_4) and xenon oxytetrafluoride (XeOF_4).

The trioxide of xenon was first prepared at Berkley University by an undergraduate. It is a white, non-volatile and highly explosive crystalline solid. It is prepared by the hydrolysis of xenon tetrafluoride or xenon-hexafluoride.

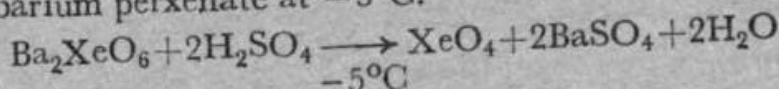


With excess of water xenon trioxide yields xenon hydroxide



Xenon trioxide crystals are orthorhombic and its molecule is trigonal pyramidal with O-Xe-O angle approximately 130° .

Xenon tetraoxide is obtained by the reduction of anhydrous sulphuric acid with barium perxenate at -5°C .



The molecule is tetrahedral (similar to periodate ion $-(\text{IO}_4^-)$ and osmium tetraoxide).

Beside these oxides, xenon also forms an oxyfluoride. Xenon oxytetrafluoride is obtained when xenon hexafluoride is made to react with glass or silica.



Another method for the preparation of this compound is the stoichiometric reaction between xenon hexafluoride and water.



At room temperature this compound is a colourless liquid which freezes to a white solid at -40°C . Spectroscopic methods reveal that its molecule is a square-based pyramid.

The future applications of these compounds are not exactly known. However, the fact that xenon forms many compounds has proved to be one of the most outstanding and stimulating observations in chemistry. It has changed our views considerably about the nature of the chemical bonds. Best of all it has challenged the octet rule which was extensively being used in the theory of valency.

The electronic formulae and structures of some inert gas compounds are given in Figs. 10.1 and 10.2.

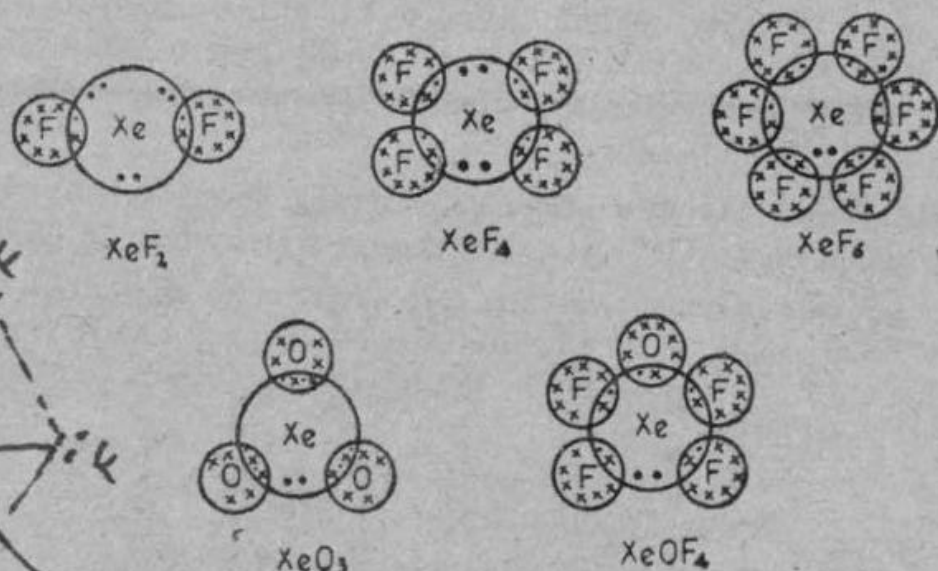


Fig. 10.1. Electronic formulae of some inert gas compounds.

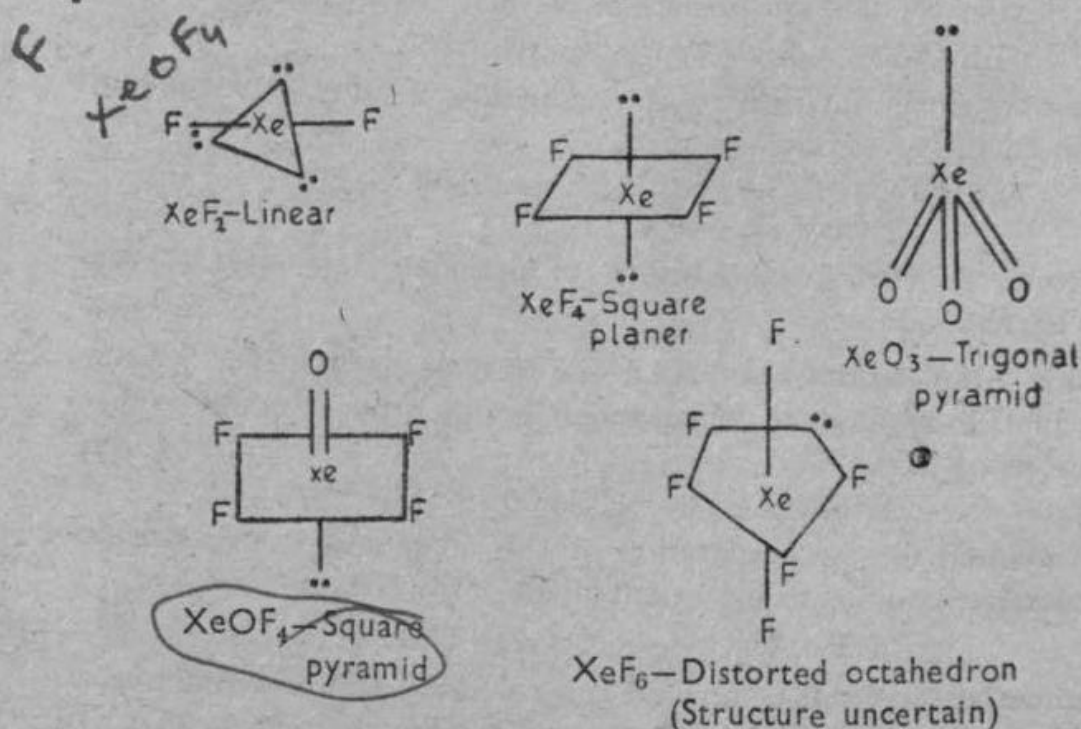


Fig. 10.2. Molecular structures of some inert gas compounds.

Questions

1. What are noble gases? Describe the electronic configuration of these elements.
2. Mention some chemical and physical properties of noble gases.
3. Write a note on the fluorides of xenon.
4. Write all you know about the compounds of noble gases.

CHAPTER 11

INTRODUCTION TO ORGANIC CHEMISTRY

The science of chemistry among other things is concerned with the various facts of how atoms are joined to form molecules. What are the chemical and physical properties of compounds, how the properties of a substance depend on its structure, how molecules are changed and modified, how an unknown substance is analyzed and its structure determined, how chemical reactions are speeded up or slowed down and how energy can be obtained from chemical reactions. With the rapid growth of chemistry in the last fifty years it has become necessary to separate this science into a number of special areas, such as physical chemistry, analytical chemistry, biochemistry, inorganic chemistry, and organic chemistry.

Historically, the term "organic chemistry" was applied to the study of those compounds, such as alcohol, sugar, and urea, that were found in living organisms but were not found in non-living matter. Indeed, for a time it was believed that organic compounds could be produced only through the agency of a "vital force" present only in living organisms. The concept of the so-called "vital force" was first discredited in 1828, when Friedrich Wohler, a German chemist, discovered that a typical organic compound, urea, previously isolated from human urine, could be prepared by heating an inorganic salt, ammonium cyanate. Subsequently many other organic compounds were prepared in the laboratory and the original definition of organic chemistry lost its significance.

Following the revolutionary discovery of Wohler, it was revealed by methods of analytical chemistry that substances of animal and plant origin, classified as organic compounds, always contained the element carbon. Although the elements hydrogen and oxygen were present in a majority of them and the elements nitrogen, halogens and

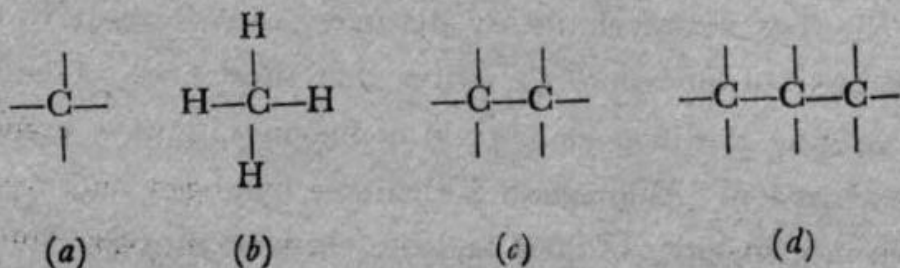
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sulphur in some of them, the element carbon was present in all of them, without exception. This led to the definition of *organic compounds* as those containing carbon, regardless of their origin. Therefore, organic chemistry today is defined as the *chemistry of the carbon compounds*. All those compounds which do not contain carbon are commonly defined as inorganic compounds.

Some carbon-containing compounds, however, are usually not studied as a part of organic chemistry. These include the carbides (e.g. CaC_2), the metal carbonates (e.g. Na_2CO_3), the metal cyanides and carbon dioxide (CO_2). These are studied with the inorganic compounds.

The question arises what is so special about carbon that a whole branch of chemistry is centered on a single element. One reason is that the compounds of carbon play a more dominant role in the chemistry of living things, both plant and animal, than those of any other element. The chemical substances which make up the tissues of our bodies, foods, dietary factors like vitamins, most of the medicines, textiles, dyes, petroleum products, plastics and synthetic fibres, perfumes and flavours, explosives, insecticides, rubber and paper are predominantly organic in nature.

The other reason why carbon compounds deserve special treatment is that the total number of known organic compounds (nearly 2 million) is more than ten times as large as known inorganic compounds. Furthermore, thousands of new organic compounds are synthesized in laboratories each year.

The carbon atom is tetravalent (has four valencies) as simply represented by (a). It may unite with four monovalent atoms (e.g. hydrogen) to give the molecule (b). It may also unite with a second carbon (c), a third carbon (d), and so on forming chains of carbon atoms :



It is seen that not only is it possible for carbon to form chains of any length, but also a given number of carbon atoms might be joined in a number of different arrangements. Thus, six carbon atoms might be linked in a variety of ways, five of which are shown below: (Fig. 11.1).

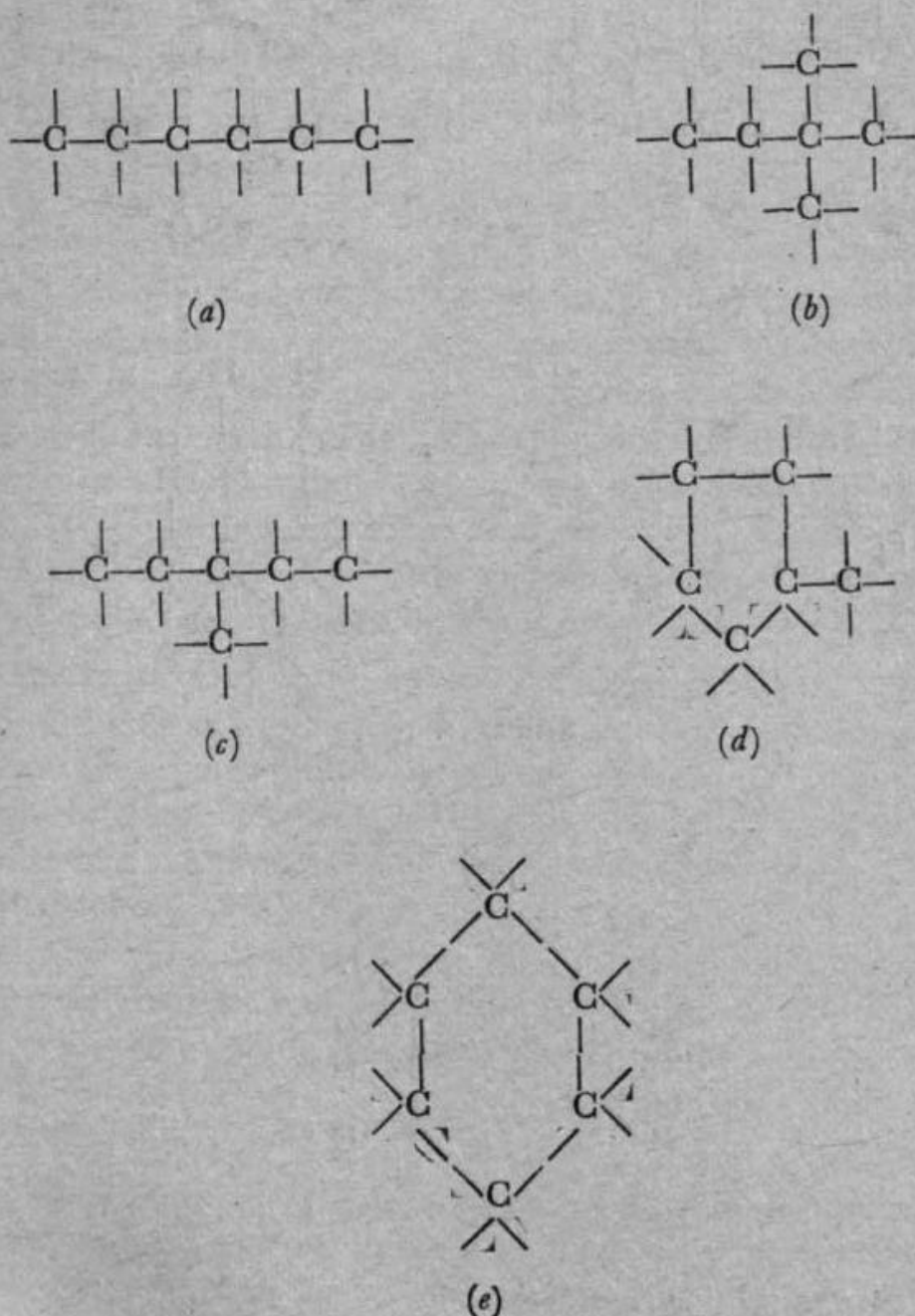


Fig. 11.1

The free valencies of the carbon atoms in Fig. 11.1 may unite with the free valencies of other atoms such as hydrogen, oxygen, nitrogen, sulphur, or halogen. Supposing that all the unfilled valencies in

Fig. 11·1 are united with hydrogen, each of the arrangements will represent a different molecule, as shown below (Fig. 11·2).

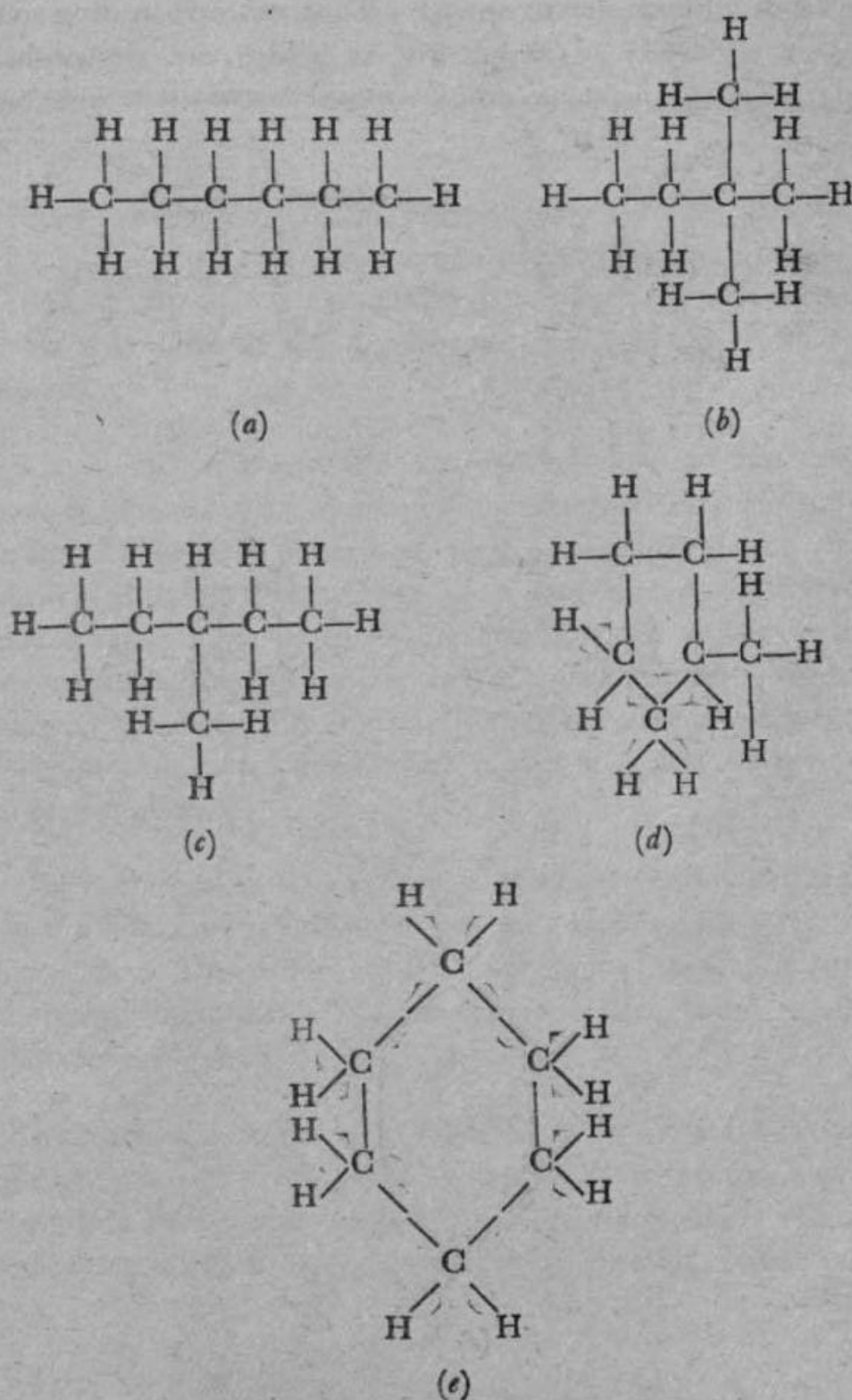


Fig. 11·2

The three compounds (Fig. 11·2—*a*, *b*, *c*) which have the same number and kind of atoms but arranged in different pattern are called, *isomers*, and each one has distinctive properties.

Thus the fact that the compounds of carbon are so numerous depends on the ability of the carbon atoms ~~to form~~ ^{to} form strong, stable covalent bonds with other carbon atoms giving rings and chains of great size, (ii) ~~to form~~ strong and stable bonds with hydrogen, oxygen and some other atoms, and (iii) ~~to form~~ isomers.

SOURCES OF CARBON AND CARBON COMPOUNDS

In a preceding paragraph, it was pointed out that foods, textiles, petroleum products, drugs, synthetic fibres, explosives, rubbers, paper and many other materials are chiefly organic in nature. Millions of tons of these materials are manufactured yearly by chemical industry, which needs enormous quantities of carbon and carbon compounds as raw materials. What are the sources from which these huge quantities of carbon and carbon compounds are obtained to serve as raw materials for the manufacture of the great variety of useful organic compounds. The principal sources of these chemical raw materials are coal, petroleum and natural gas.

Coal : Coal, a black mineral of vegetable origin, exists in the form of seams at varying depths under the earth's surface. Millions of years ago, warm and wet climatic conditions promoted rapid growth of trees. The accumulation and burial of the decaying trees in successive layers gave rise to vast deposits, which, under the influence of temperature, pressure and time, changed into hard beds of coal. The main constituent of coal is carbon with smaller amounts of hydrogen, oxygen and nitrogen and minor amounts of sulphur. The hardest coal, anthracite, may contain 85-90% of carbon, while the softest coal, peat, still contains unchanged plant remains and may not contain more than 50-60% carbon.

When coal is heated to high temperature in the absence of air, coaltar and coal gas are distilled off from coal while a residue, called coke, remains. 1000 kg. of coal gives about 680 kg. of coke, 45 kg. of coaltar and 28300 cubic meters of coal gas. Coke is used in the manufacture of steel and calcium carbide, whereas coaltar and coal gas yield commercial quantities of many organic compounds such as benzene, toluene, xylenes, phenol, cresols and naphthalene. Calcium carbide (CaC_2) is used in the manufacture of acetylene from which many other organic compounds can be made.

Petroleum and Natural Gas : Natural gas and petroleum are also believed to have been formed by the decomposition of living matter over millions of years and the accumulation of these decomposition products in porous formations capped by rock. When a well is drilled through the cap, natural gas escapes and, for a time, oil is forced, to the surface by the gas pressure. After the pressure has subsided, the oil must be pumped out of the well.

The chief constituents of natural gas are low molecular weight compounds of carbon and hydrogen from which almost any organic compound can be prepared. There are vast reserves of natural gas in Pakistan (*e.g.* at Sui). Although at present Sui gas is mostly used as fuel, it could be exploited as a very valuable raw material for the manufacture of an unlimited number of important organic compounds.

Petroleum is a mixture of solid, liquid and gaseous compounds of carbon and hydrogen with smaller proportions of sulphur, nitrogen and oxygen compounds. It is not only a source of fuels but products of petroleum refining are employed for the manufacture of alcohols, ketones, ethers and numerous other substances known as "petrochemicals".

In addition, plants and animals are themselves sources of many useful organic compounds such as sugars, starches, vegetable oils, dyes, drugs, fibres and animal fats.

STRUCTURAL FORMULAS OF ORGANIC COMPOUNDS

The study of an organic compound after it has been obtained in a pure state, begins with the detection of elements present in it. After identifying the elements present, the percentage of each is determined. From the percentage composition the empirical formula of the compound is calculated. A formula which indicates the relative number of different kinds of atoms in a molecule is called an *empirical formula*. The next stage in the investigation is to determine the molecular weight of the compound. From the *empirical formula* and the molecular weight of a compound, its molecular formula is derived. *Molecular formula* tells the actual number of each kind of atoms in a molecule.

The molecular formula of a compound does not tell how the various atoms present are arranged in the molecule of that compound. The arrangement of atoms in a molecule is indicated by writing a

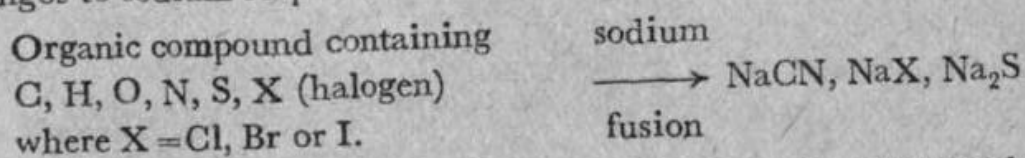
structural formula. After the molecular formula has been established, the chemical properties of the compound are studied to determine the relative positions of atoms in the molecule. A structural formula is then written keeping in mind the postulates of the structural theory of Kekule (1859), a German chemist. According to this simple but very important theory each carbon atom in the molecule has a normal valency of four, hydrogen and halogens have a valence of one, oxygen and sulphur a valence of two, and nitrogen a valence of three.

Each of the above stages in the chemical investigation of an organic compound is discussed as follows :

(1) **Detection of Elements :** All organic compounds contain carbon and almost all contain hydrogen. The presence of carbon and hydrogen is indicated by the formation of carbon dioxide and water, when a small sample of the compound is heated to red heat in the presence of copper oxide. The combustion of the sample over copper oxide in this manner converts the carbon into carbon dioxide and the hydrogen into water. Carbon dioxide turns lime water milky and the water vapours turn white anhydrous copper sulphate blue.

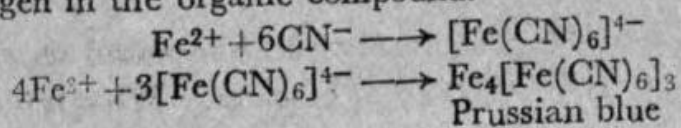
The presence of other elements which are generally nitrogen, sulphur and the halogens, is commonly detected by what is known as the *sodium fusion* test. In this method, a small amount of the organic compound is mixed with a tiny piece of sodium metal, and then heated to redness in a small test tube.

Nitrogen is thus converted into sodium cyanide (NaCN), sulphur changes to sodium sulphide and the halogens to sodium halides :

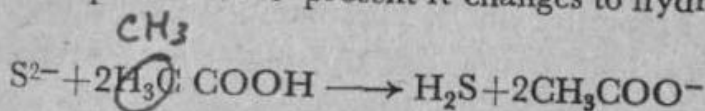


The contents of the red hot tube are dissolved in water and the water solution divided into several portions. Each portion is then tested for one of the expected ions (CN⁻, S²⁻, X⁻) as follows :

Nitrogen Test : One portion of the above solution is made alkaline and to it ferrous sulphate solution is added. On boiling, and acidification a blue precipitate of ferric ferrocyanide (Prussian blue) appears, showing the presence of cyanide ion in the solution and hence nitrogen in the organic compound.



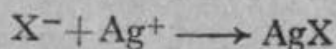
Sulphur Test : Another portion of the solution is acidified with acetic acid. If sulphide ion is present it changes to hydrogen sulphide (H_2S).



The acidified solution is boiled to drive off H_2S gas, which turns a piece of filter paper dipped in lead acetate solution black.



Halogen Test : The halide ion (Cl^- , Br^- , I^-) is tested by boiling a third portion of the solution with nitric acid to remove cyanide ion and sulphide ion and then adding an aqueous solution of silver nitrate. If a halogen is present, a precipitate is formed. The precipitate is white if chlorine is present, pale yellow if bromine is present and deep yellow if iodine is present.



(2) Determination of the Percentage Composition—Carbon and Hydrogen : A weighed amount of the organic compound is heated in a test tube with copper oxide in a 1 m. long combustion tube filled with copper oxide. The carbon dioxide evolved is absorbed in a small bulb containing potassium hydroxide, which has been previously weighed. The potassium hydroxide bulb is weighed again after it has absorbed the evolved carbon dioxide. From the increase in weight of the potassium hydroxide bulb, the percentage of carbon in the sample is calculated as follows :

$$\% \text{C} = \text{Wt. of CO}_2 \times \frac{12.01}{44.01} \times \frac{100}{\text{wt. of sample}}$$

In the same experiment, any hydrogen present in the organic compound will form water, which may be absorbed in a weighed tube of calcium chloride. The gain in weight of the calcium chloride tube is due to the weight of water formed. The percentage of hydrogen in the sample is, then, calculated as follows :

$$\% \text{H} = \text{Wt. of H}_2\text{O} \times \frac{2.016}{18.020} \times \frac{100}{\text{wt. of sample}}$$

18.016

Example : 0.01650 g. of an organic compound on analysis gave 0.03153 g. carbon dioxide and 0.01937 g. water. What is the percentage

of carbon and hydrogen in the compound? (C=12.01, H=1.008, O=16.00).

$$(a) \text{ wt. of C in the sample} = \text{wt. of CO}_2 \times \frac{\text{At. wt. of C}}{\text{Mol. wt. of CO}_2}$$

$$\begin{aligned} \%C &= \frac{\text{wt. of CO}_2}{\text{wt. of sample}} \times \frac{12.01}{44.01} \times 100 \\ &= \frac{0.03153}{0.01650} \times \frac{12.01}{44.01} \times 100 = 52.14\% \end{aligned}$$

$$\begin{aligned} (b) \text{ wt. of H}_2 \text{ in the sample} &= \text{wt. of H}_2\text{O} \times \frac{\text{Mol. wt. of H}_2}{\text{Mol. wt. of H}_2\text{O}} \\ &= \text{wt. of H}_2\text{O} \times \frac{2.016}{18.016} \end{aligned}$$

$$\begin{aligned} \%H &= \frac{\text{wt. of H}_2\text{O}}{\text{wt. of sample}} \times \frac{2.016}{18.016} \times 100 \\ &= \frac{0.01937}{0.01650} \times \frac{2.016}{18.016} \times 100 = 13.13\%. \end{aligned}$$

Nitrogen : A general method for the quantitative determination of nitrogen consists in heating a weighed sample of the organic compound over copper oxide in a glass tube in which the air has been displaced by carbon dioxide. The nitrogen forms oxides of nitrogen and the carbon changes to carbon dioxide. The oxides of nitrogen are reduced to nitrogen by passing over a heated copper gauze.

The volume of nitrogen produced is measured by collecting it in a graduated cylinder over 50 percent aqueous potassium hydroxide, which absorbs the carbon dioxide. The temperature and the barometric pressure is noted. The volume of nitrogen is corrected to standard conditions of temperature and pressure (S. T. P.; 0° and 760 mm), by the application of the gas laws. From these data the weight of nitrogen and its percentage in the sample is calculated. This is called the *Dumas method*.

Example : 0.00865 g. of an organic nitrogen compound when analyzed by the Dumas method gave 1.80 ml of nitrogen collected at 25° and 739 mm over 50 percent potassium hydroxide. (Vapour pressure of water over 50 percent potassium hydroxide at 25°C is 9 mm).

$$\begin{aligned} \text{Corrected volume of nitrogen} &= 1.80 \times \frac{739-9}{760} \times \frac{273}{298} \\ &= 1.59 \text{ ml} \end{aligned}$$

wt. of nitrogen in 0.00865 g. of sample

$$= 1.59 \times \frac{28.02}{22.4 \times 1000} = 0.00199 \text{ g.}$$

$$\% \text{ nitrogen in the sample} = \frac{0.00199}{0.00865} \times 100 = 23\%$$

In another procedure, the *Kjeldahl method*, a weighed sample of the organic compound is heated with concentrated sulphuric acid and an oxidizing agent such as mercuric oxide. The nitrogen in the sample is converted into ammonium sulphate. The reaction mixture is diluted with water and then treated with sodium hydroxide to convert the ammonium sulphate to ammonia. The ammonia is distilled into a known volume of standard acid. The quantity of standard acid left unused is then found by titration against a standard alkali. From this the percentage of nitrogen in the compound can be calculated.

Example : 1.525g. of an organic nitrogen compound was decomposed and distilled with NaOH in a Kjeldahl experiment. NH_3 was collected in 30 ml. of N-hydrochloric acid. The remaining acid required 120 ml. decinormal NaOH for complete neutralization. Calculate % of N_2 .

$$\begin{aligned} \text{Volume of N/10 NaOH employed for neutralization} \\ = 120 \text{ ml.} \end{aligned}$$

$$\therefore \text{Volume of N NaOH employed for neutralization} \\ = 12.0 \text{ ml.}$$

$$\begin{aligned} \text{Hence volume of N-HCl neutralized by } \text{NH}_3 &= 30 - 12 \\ &= 18.0 \text{ ml.} \end{aligned}$$

$$\begin{aligned} \therefore \text{wt. of } \text{N}_2 \text{ in 1.525 g. of the substance} \\ = \frac{14}{1000} \times \frac{18}{1} = \frac{252}{1000} \text{ g.} \end{aligned}$$

$$\% \text{ of } \text{N}_2 \text{ in the compound} = \frac{252}{1000} \times \frac{100}{1.525} = 16.4\%.$$

Estimation of Oxygen : The percentages of all the other elements present in a compound are added. If the sum of these is equal to 100, oxygen is taken to be absent. If the sum of all other percentages is less than 100, then the difference is the percentage of oxygen.

(3) Determination of the Empirical Formula : The determination of the empirical formula from the percentage composition involves steps which are illustrated by the following example :

Example : A compound has the following analysis :
 $C=48.64\%$, $H=8.16\%$, O (by difference) $=43.20\%$, calculate its empirical formula. Atomic weights are, $C=12.01$, $H=1.008$, $O=16.00$.

(a) Divide the percentage of each element by its atomic weight :

$$C : \frac{48.64}{12.01} = 4.05$$

$$H : \frac{8.16}{1.008} = 8.09$$

$$O : \frac{43.20}{16.00} = 2.70$$

(b) Divide each resulting number (quotient) by the smallest :

$$C : \frac{4.05}{2.70} = 1.5$$

$$H : \frac{8.09}{2.70} = 3.0$$

$$O : \frac{2.70}{2.70} = 1.0$$

(c) Convert the quotients from step (b) to whole numbers :

$$C = 1.5 \times 2 = 3$$

$$H = 3.0 \times 2 = 6$$

$$O = 1.0 \times 2 = 2$$

The empirical formula of the compound is $C_3H_6O_2$. Thus the simplest ratio in which the atoms of carbon, hydrogen and oxygen are present in the organic molecule is 3 : 6 : 2.

(4) Molecular Weight : The molecular weight of an organic compound may be determined by one of the several methods. The most commonly used are the *boiling point elevation* (ebullioscopic) method and the *freezing point depression* (cryoscopic) method. The principle on which these methods are based is that the lowering of the freezing point or the elevation of the boiling point of a solvent is very nearly proportional to the number of moles of solute in a fixed weight of the solvent. Conventionally, 1000 grams of solvent is used as a basis. Thus when one gram molecular weight of a solute is dissolved in 1000 grams of a solvent, there is a *fixed* elevation in the boiling point of the solvent and a *fixed* lowering in the freezing point of the solvent. *The elevation in boiling point and the depression in freezing point depend on the nature of the solvent and not on the nature of solute, provided the solute does not dissociate or associate in the solvent.* Thus, for example, whenever one gram

molecular weight of *any nonelectrolyte* is dissolved in 1000 grams of water, a boiling point elevation of 0.52° and a freezing point depression of 1.86° occurs. 0.52° is called the *molal boiling point constant* of water and 1.86° is its *molal freezing point constant*. The molal boiling point constant (ebullioscopic constant) of a solvent is equal to the elevation in boiling point of the solvent caused by dissolving one gram molecular weight of a solute in 1000 grams of the solvent. The molal freezing point constant (cryoscopic constant) is similarly defined.

These constants have been determined for a number of solvents by using solutes of known molecular weight.

For finding out the molecular weight of an unknown organic compound, a given weight of the compound is dissolved in a known weight of an organic solvent. The boiling point or the freezing point of the solution is noted. The boiling point of the pure solvent is subtracted from the boiling point of the solution to obtain the observed elevation in boiling point. Similarly, the freezing point of the solution is subtracted from the freezing point of the pure solvent and the observed depression in freezing point obtained. The molecular weight of the organic solute is then calculated as follows :

$$\text{Molecular weight} = \frac{K_b}{\Delta t} \times \frac{\text{weight of compound}}{\text{weight of solvent}} \times 1000$$

where K_b = the molal boiling point constant of the solvent, and

Δt = the observed elevation in boiling point (in $^{\circ}\text{C}$). Similarly,

$$\text{Molecular weight} = \frac{K_f}{\Delta t} \times \frac{\text{weight of compound}}{\text{weight of solvent}} \times 1000$$

where K_f = the molal freezing point constant of the solvent, and

Δt = the observed depression in freezing point (in $^{\circ}\text{C}$).

The K_b and K_f values for several organic solvents useful in molecular weight determinations are listed below :

Solvent	B.P. $^{\circ}\text{C}$	K_b	Freezing Point $^{\circ}\text{C}$	K_f
Water	100	<u>0.52</u>	0	1.86
Acetic acid	118	3.07	16.7	3.86
Benzene	80	2.53	5.5	5.12
Cyclohexane	81	2.79	6.5	20.0
Camphor	..	..	178.4	37.7

Example : 0.333 g. of an organic compound was dissolved in 10 g. of acetic acid. The freezing point of the solution was 14.86°C whereas the freezing point of pure acetic acid is 16.7°C . The molal freezing point constant for acetic acid is 3.86. Calculate the molecular weight of the organic compound.

$$K_f = 3.86; \Delta t = (16.70 - 14.86) = 1.84^{\circ}\text{C}$$

$$\therefore \text{Mol. wt.} = \frac{3.86}{1.84} \times \frac{0.333}{10.00} \times 1000 = 69.8.$$

The values of molecular weights obtained by the ebullioscopic or the cryoscopic method are usually in error upto about $\pm 10\%$. However, the values thus obtained are good enough for deriving correct molecular formulas from the accurately determined empirical formulas.

(5) Molecular Formula : The molecular formula of a compound is derived from its empirical formula and its molecular weight as shown below :

Suppose the empirical formula of a compound is determined to be CH_2O . Its molecular formula will be $(\text{CH}_2\text{O})_n$, where $n = 1, 2, 3, \dots$ etc.

The value of n is found by dividing the molecular weight by the empirical formula weight. If the molecular weight of the above compound = 60, then

$$n = \frac{\text{molecular weight}}{\text{empirical formula weight}} = \frac{60}{30} = 2$$

Therefore the molecular formula is $(\text{CH}_2\text{O})_2$ or $\text{C}_2\text{H}_4\text{O}_2$.

If the molecular weight were found to be 90, then $n = \frac{90}{30} = 3$,

and the molecular formula $(\text{CH}_2\text{O})_3$ or $\text{C}_3\text{H}_6\text{O}_3$.

Note that n is always a whole number. If the value obtained from given data is fractional, due to experimental error in mol. wt. determination, the nearest whole number should be used. Thus if the ratio

$$\frac{\text{mol. wt.}}{\text{E. F. wt.}} = 1.90, n \text{ is taken} = 2.$$

In organic chemistry two or more than two compounds may have the same molecular formula. Such compounds are said to be isomeric with each other. For example, if the molecule of an unknown compound

is found to be C_2H_6O , it can have the arrangement of atoms as shown in 11.3a or as shown in 11.3b. Both of these formulas satisfy the condition that carbon has a valence of four, oxygen two and hydrogen one.

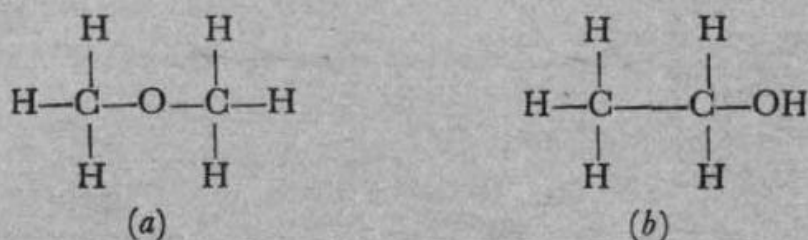
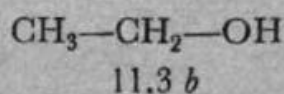
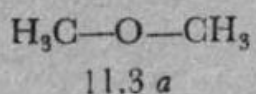


Fig. 11.3

The structure 11.3a represents an ether and 11.3b is the structural formula of an alcohol. The properties of 'a' depend largely on the group C-O-C and the properties of 'b' depend on the group, —OH. After establishing the molecular formula, C_2H_6O , a study of the chemical reactions of the compound will show whether the given compound has the structure '3a' or structure '3b'. Thus, often it is not enough to know only the molecular formula to characterize a compound completely. The arrangement of the different kind of atoms in the molecule, i.e., its structural formula, must be determined by a study of the chemical properties of the unknown compound.

The organic chemists usually write abbreviated structural formulas. For example, the structures 11.3a and 11.3b are written as :

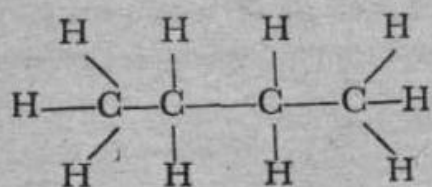


CLASSIFICATION OF ORGANIC COMPOUNDS

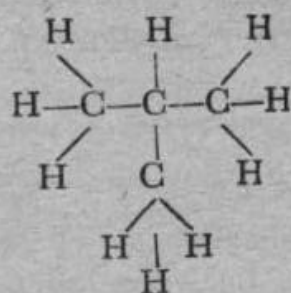
Earlier it was mentioned that the number of known organic compounds, nearly two million, is much larger than the total number of the compounds of all other elements. This is due to (1) the ability of a carbon atom to combine with four atoms or groups of atoms, (2) the fact that carbon atoms can combine with each other indefinitely to form chains and rings which are stable, and (3) the existence of isomerism in organic compounds. The framework⁽¹⁾ of carbon atoms on which a molecule is built is called the carbon skeleton of the compound.

The carbon skeleton of an organic compound may consist of an *open chain* of carbon atoms, continuous or branched, or it may be in the form of a *closed chain*—a ring. The open chain compounds are

called *acyclic* or *aliphatic*, whereas the closed chain or ring compounds are called *cyclic* compounds, *e.g.* (Fig. 11.4).

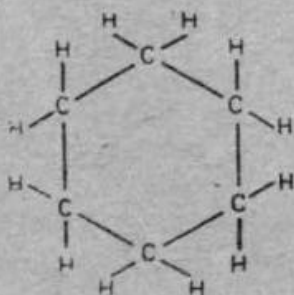


An acyclic compound
(The carbon chain is continuous)



An acyclic compound
(The carbon chain is branched)

Cyclic compounds containing rings made up of only carbon atoms are called *carbocyclic* or *homocyclic* compounds. Carbocyclic compounds containing at least one benzene ring in their molecule are called *aromatic*; others are called *nonbenzenoid* compounds. A benzene ring is made up of six carbon atoms with three alternative double bonds in it, Fig. 11.5.

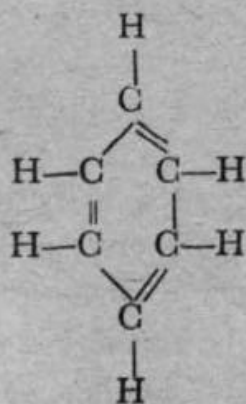


usually written as

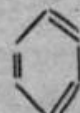


Cyclohexane
(A nonbenzenoid carbocycle)

Fig. 11.4



usually written as



Benzene
(An aromatic carbocycle)

Fig. 11.5

When a cyclic compound contains a ring which is made up of more than one kind of atoms, the compound is called a *heterocyclic* compound. Usually a heterocyclic ring is made up of several carbon atoms and one or more than one atoms of other elements such as nitrogen, sulphur or oxygen. The N, S or O are called hetero-atoms. Examples of simple heterocyclic compounds are (Fig. 11.6).

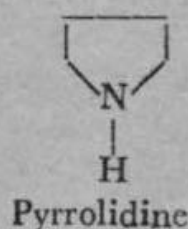
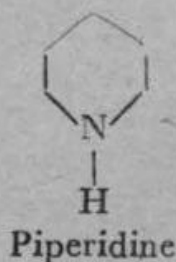
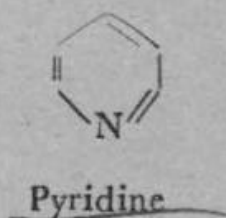
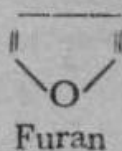
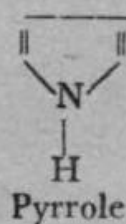
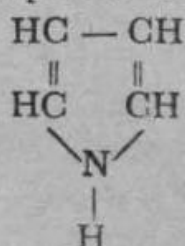
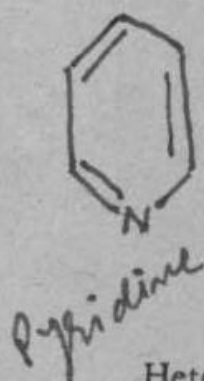


Fig. 11.6



Heterocyclic compounds which have two double bonds in a five membered ring or three double bonds in a six membered ring are also aromatic in character like the compounds containing a benzene ring.

The organic compounds are, therefore, divided into the following main classes according to the nature of their carbon skeleton :

- (1) aliphatic,
- (2) aromatic,
- (3) nonbenzenoid carbocyclic, and
- (4) heterocyclic compounds.

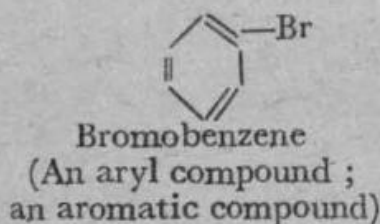
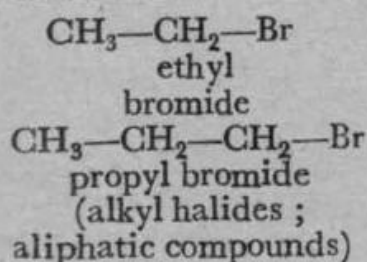
The number of organic compounds belonging to each of the above classes is so large that a study of the methods of preparation, and the physical and chemical properties of each compound as an individual would be impossible. Fortunately, it is possible to divide them further into a relatively smaller number of families of compounds. The members of each family have important structural features common to them. Therefore, their methods of preparation and chemical properties are similar and their physical properties vary

gradually. Thus, it is not necessary to study each member of a family individually. Instead a typical member of the family may be studied. The behaviour of other members of the family is then predictable.

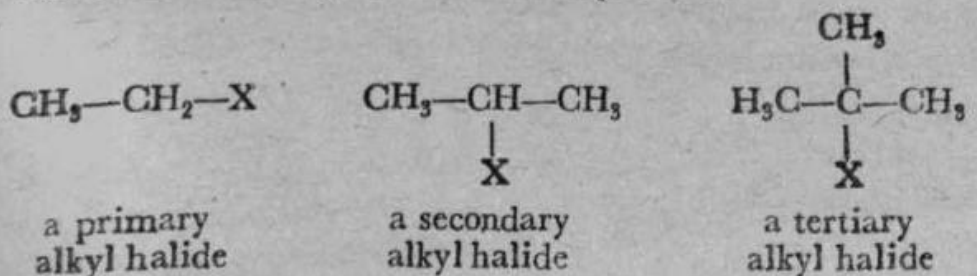
Functional Groups : The important properties of each family of compounds depend on what is known as a *functional group*. An atom or a group of atoms which confers characteristic properties to an organic molecule is called a *functional group*. Usually, the remainder of the molecule is not involved in most of the characteristic reactions of the compound. A brief discussion of the commonest groups of atoms that are responsible for the characteristic reactions of organic compounds is given below :

COMMON FUNCTIONAL GROUPS

(1) The *C-X group*, C-Cl, C-Br, or C-I, is the characteristic group present in the family of compounds called the *alkyl halides* and *aryl halides*. Typical members of these families are :



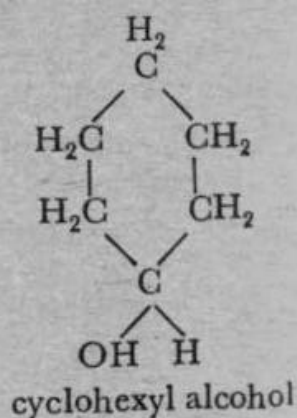
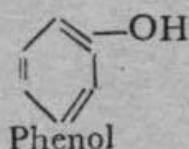
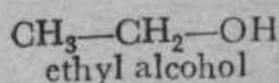
It may be pointed out here that the carbon atom to which a functional group is attached may be primary, secondary or tertiary. A *primary* carbon atom is that which is directly bonded to one other carbon atom. A *secondary* carbon atom is that which is directly attached with two other carbon atoms, while a *tertiary* carbon atom is directly bonded to three other carbon atoms. Therefore, if the halogen atom in an alkyl halide is attached with a primary carbon atom, it is called a primary alkyl halide, and when the halogen atom is bonded to a secondary carbon atom the compound is called a secondary alkyl halide. Similarly, if the halogen atom is linked with a tertiary carbon atom, the compound is called a tertiary alkyl halide. Examples are :



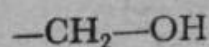
Thus all the primary alkyl halides contain the group $-\text{CH}_2-\text{X}$, secondary alkyl halides contain the group $\text{>CH}-\text{X}$ and tertiary alkyl halides contain the group $\text{>C}-\text{X}$.

carbon atom of

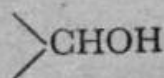
(2) **The Hydroxyl Group :** $-\text{O}-\text{H}$, is the characteristic group present in two large classes of compounds called *alcohols* and *phenols*. Phenols have the $-\text{OH}$ group directly bonded to a benzene ring, whereas in alcohols the $-\text{OH}$ group is linked with the carbon atom of an open chain or a nonbenzenoid cyclic compound. Examples are as follows :



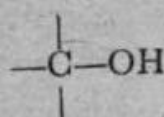
Alcohols, like the alkyl halides, are also classified into primary, secondary, and tertiary alcohols. Thus the typical groups of the three types of alcohols are :



primary alcohol
group

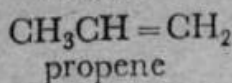
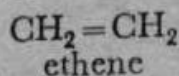


secondary alcohol
group

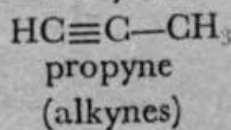
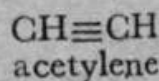


tertiary alcohol
group

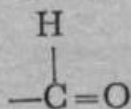
(3) **The Olefinic Double Bond,** $\text{C}=\text{C}$, and the *acetylinic triple bond*, $\text{C}\equiv\text{C}$. The family of compounds whose members contain the functional group, $\text{C}=\text{C}$, are called *olefins* or *alkenes* and the family of compounds whose members contain the group, $\text{C}\equiv\text{C}$, are called *alkynes*. Typical examples are :



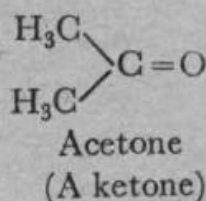
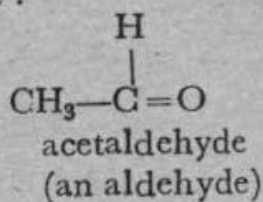
(olefins or alkenes)



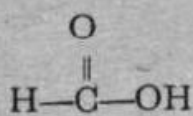
(4) **The Carbonyl Group**, >C=O , is the functional group of *aldehydes* and *ketones*. In aldehydes the >C=O is directly linked with at least one hydrogen atom, i.e., the group.



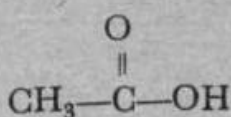
is present in all compounds called aldehydes. In ketones the >C=O group is directly linked to two carbon atoms. Examples of aldehydes and ketones are :



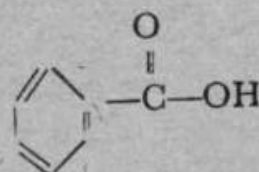
(5) **The Carboxyl Group** : $-\text{C}(=\text{O})\text{OH}$, which consists of a carbonyl group and a hydroxyl group directly joined in a single unit, is the characteristic group of a class of compounds called the *carboxylic acids*. Examples are :



Formic acid

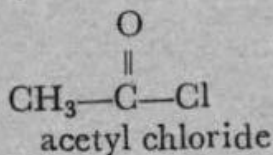


Acetic acid

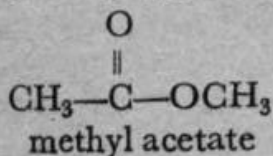


Benzoic acid

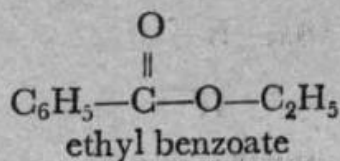
When the OH group of a carboxylic acid is replaced by a chlorine atom, the functional group $-\text{C}(=\text{O})\text{Cl}$ is obtained. Compounds containing this functional group are called *acid chlorides*, e.g. :



Replacement of the hydrogen atom of the carboxylic group by a group such as CH_3 or C_2H_5 gives an *ester*.



(an ester of acetic acid)

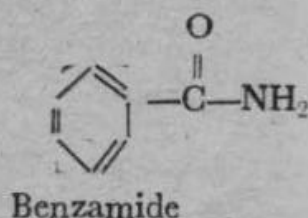
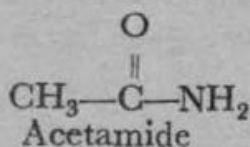
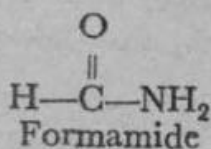


(an ester of benzoic acid)

Thus the functional group —CO OR (where $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5$ or C_3H_7 and so on) is the characteristic group of *esters*.

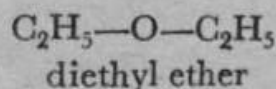
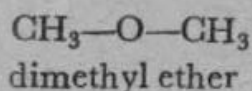
If the —OH group of the carboxyl group is replaced by —NH_2

group, the new group, $\text{—}\overset{\text{O}}{\parallel}\text{C—NH}_2$ is called an amide group. All compounds which contain this functional group are called *amides*.

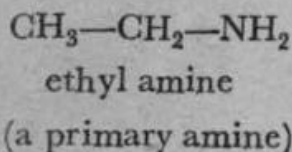


Esters, acid chlorides and amides may be regarded as derivatives of carboxylic acids.

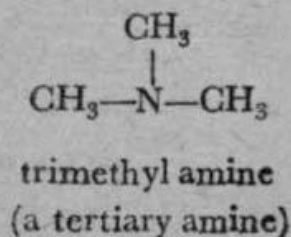
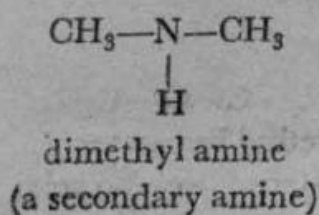
(6) **The Ether Linkage :** C—O—C group, is the functional group of the class of compounds called *ethers e.g.,*



(7) **The Amino Group :** —NH_2 is present in the family of compounds called *amines*. All compounds which have an —NH_2 group linked with a carbon atom are called *primary amines, e.g.,*



When in a compound an —NH group is directly attached with two carbon atoms, the compound is called a *secondary amine*, and if a nitrogen atom —N— is directly linked with three carbon atoms, the compound is called a *tertiary amine*. Examples are :



Questions

1. Differentiate clearly between empirical and molecular formula. Is it possible for a compound to have identical empirical and molecular formulas ?
2. Write down the structural formulas of the two isomeric aliphatic compounds having the molecular formula C_2H_6O .
3. Metal halides, usually, form a white precipitate with $AgNO_3$ solution, but alkyl halides do not. Explain.
4. Give a satisfactory definition and example for each of the following terms :—
 - (a) functional group,
 - (b) molecular formula,
 - (c) structural formula,
 - (d) hydrocarbon,
 - (e) secondary carbon,
 - (f) tertiary carbon.
5. Write down the structural formulas for the following :—
 - (a) an alcohol,
 - (b) an aldehyde,
 - (c) a primary amine,
 - (d) a tertiary amine,
 - (e) a carboxylic acid.
6. Why is it necessary to burn organic compounds with sodium metal before the presence of elements in the compound could be detected ?
7. 30 grams of an organic compound gave on combustion 88 g of CO_2 and 54 g of water. Calculate the percentage of carbon and hydrogen in it. (Ans. C=80%, H=20%)
8. 0.2475 g of a substance gave on combustion 0.4950 g of carbon dioxide and 0.2025 g of water. Find out the percentage of carbon and hydrogen in it. (Ans. C=54.5%, H=9.09%)
9. 0.1877 g of an organic compound when analysed by Duma's method yielded 29.6 cc of nitrogen at S. T. P. Determine the percentage of nitrogen in the substance. (Ans. N=19.71%)

10. 0.257 g of an organic compound was heated with strong H_2SO_4 and then distilled with strong alkali. The ammonia evolved was absorbed in 50 ml of N/10 HCl which required 23.2 ml of N/10 NaOH for neutralization at the end of operation. Find out the percentage of nitrogen in the compound.
(Ans. N = 14.59%)
11. 0.512 g of an organic compound when dissolved in 25 g of water lowered its freezing point by 0.19° . Calculate the molecular weight of the substance. Molecular depression constant for water is 1.85° .
(Ans. 199.4)
12. 0.440 g of a substance dissolved in 22.2 g benzene lowered the freezing point of benzene by 2.567° . Calculate the molecular weight of the substance. (Molecular depression constant for benzene $K_f = 5.12$).
(Ans. 39.8)
13. The boiling point of pure acetone is 56.38° at normal pressure. A solution of 0.717 g of a compound in 10 g of acetone boiled at 56.88° . What is the molecular weight of the compound? (The molecular elevation constant for acetone is 1.67).
(Ans. 239.5)
14. The boiling point of chloroform was raised by 0.323° , when 0.5143 g of anthracene was dissolved in 35.0 g of chloroform. Calculate the molecular weight of anthracene. (Molecular elevation constant for chloroform $K_b = 3.85$).
(Ans. 175.2)
15. An organic substance on analysis was found to contain 10.06% carbon, 0.84% hydrogen and 89.0% of chlorine. Calculate its empirical formula.
(Ans. CHCl_3).
16. An organic liquid contains 12.8% carbon, 2.1% hydrogen, 85.1% bromine. 0.188 g of the compound on combustion displaced 22.4 ml of dry air at S. T. P. Find out the molecular formula of the substance. (22.4 liter of gas at S.T.P. $\equiv$ one gram molecule).
(Ans. $\text{C}_2\text{H}_4\text{Br}_2$)
17. In the sodium fusion method for the detection of halogens in compounds containing nitrogen or sulphur, the solution must be boiled after acidification with nitric acid before adding silver nitrate. Explain why?

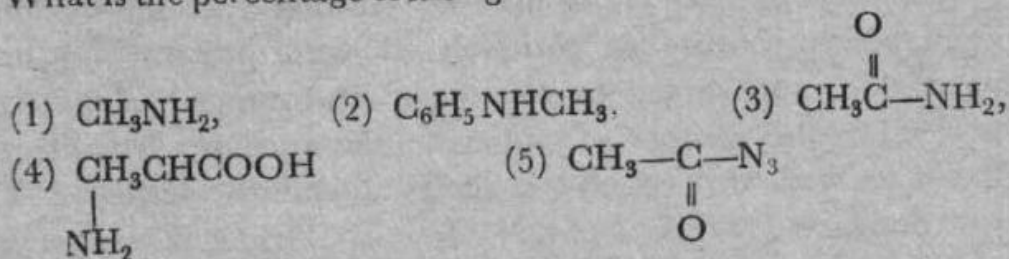
18. How many grams of each of the following compounds must be burned to give 4.40 g of carbon dioxide?

(a) C_2H_6O , (b) C_2H_4 , (c) $C_6H_{12}O_6$, (d) C_2H_6 , (e) $CHCl_3$,

(Ans. (a) 2.3g; (b) 1.49g; (c) 3.0g; (d) 1.5g; (e) 11.95g.)

19. What is the minimum possible molecular weight of a compound that contains 31.56% bromine? (Ans. 253.48)

20. What is the percentage of nitrogen in each of the following?



(Ans. (1) 45.16%; (2) 13.08%; (3) 23.73%; (4) 15.73%;
 (5) 49.41%.

21. An organic compound containing only carbon, hydrogen and oxygen was found to have $C=75.20\%$, and $H=10.75\%$. Its molecular weight was found to be about 115. Chemical analysis showed that it contained a carbonyl group ($>C=O$). Write a structure of the compound.

22. An organic compound, A, was found to contain :

$C=49.3\%$, $H=9.6\%$, $N=19.2\%$, $O=21.9\%$.

A solution of 0.1825 g of the substance in 10.00 g of water began to freeze at $-0.465^\circ C$. What are the empirical and molecular formulas of the compound? (Molecular freezing point depression constant for water is 1.86). (Ans : C_3H_7NO)

CHAPTER 12

THE NATURE OF THE CHEMICAL BOND

Various THE TYPES OF CHEMICAL BOND

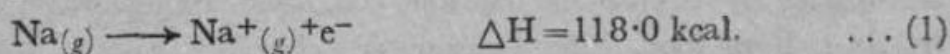
The various types of chemical bonds were discussed in Chapter 5 of "Chemistry" Part I. It may be recalled that the nucleus of an atom which consists of positively charged protons and uncharged neutrons, is surrounded by electrons. The number of these electrons is equal to the number of protons in the nucleus. The electrons are found in successive concentric shells around the nucleus. The shells are designated as K, L, M, N, O, etc. The maximum number of electrons that a shell can contain is given by the formula $2n^2$, where n is the number of the shell. Thus the first shell (K shell), which is nearest to the nucleus, will accommodate a maximum of 2 electrons, the second (L shell) 8 electrons and the third (M shell) 18 electrons. The outermost shell (except in He) can have a maximum of 8 electrons only.

Atoms of the rare gases, He, Ne, Ar, Kr, Xe, and Rn, have completely filled outer shells and are generally chemically inert. Atoms, whose outer shells are not completely filled, are chemically reactive. They form bonds with other atoms either by transference of electrons (ionic bond or electrovalent bond) or by sharing of electrons (covalent bond) and in the process acquire the electronic configuration of the nearest rare gas which has a complete outer shell of 8 electrons (the Octet rule, first postulated by W. Kossel and G. N. Lewis in 1916) except in the case of helium in which 2 electrons complete the first shell.

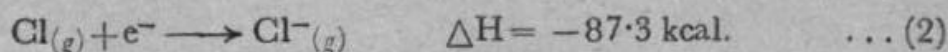
The ionic bond is usually formed between the elements of groups I and II and those of groups VI and VII of the periodic table because the I and II group elements have relatively low ionization potentials and the elements of Groups VI and VII have relatively high electron affinities. Consider the process of bond formation between an element of Group I, e.g., sodium, and an element of Group VII, e.g., chlorine. The sodium atom has one electron in its outer shell, whereas the chlorine atom has seven electrons in the outer shell. They will form a bond by complete transference of the outer electron of sodium to the outer shell of chlorine, which will then have a

completed outer shell of eight electrons. The sodium atom will change to Na^+ and the chlorine atom to Cl^- . Na^+ has the electronic configuration of the nearest rare gas, neon, whereas Cl^- has the electronic configuration of the nearest rare element argon. Since particles carrying opposite charges attract each other, these ions are held together by electrostatic attractions. This type of bond is called *ionic bond* or *electrovalent bond*.

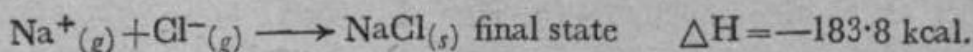
In order to understand why this electron transfer takes place readily, it will be instructive to consider the energy changes involved. The removal of the outer electron from the attractive influence of the positively charged sodium nucleus requires energy = 118.0 kcal, mole⁻¹ (ionization potential of sodium = 5.1 electron-volts)



This loss of energy is only partially compensated (not "more than compensated") when the outer shell of chlorine is filled, releasing 87.3 kcal. of energy, corresponding to the electron affinity of chlorine (3.75 ev.)



The remaining energy loss (118.0 - 87.3 = 30.7 kcal.) is more than compensated when the oppositely charged ions form a crystal lattice consisting of a closely packed array of the two ions, in which each sodium ion is surrounded by six chloride ions and each chloride ion is surrounded by six sodium ions. The forces of attraction between the oppositely charged ions in the lattice greatly decrease the energy of the system.



It follows from this discussion that (1) the statement, "sodium atom readily loses its outer electron to acquire the *stable* electronic configuration of the nearest rare gas or to complete its octet" is erroneous, because it requires a great deal of energy (118.0 kcal. mole⁻¹) to change Na to Na^+ . Na^+ is less stable than Na by 118.0 kcal. mole⁻¹. The fact is that the conversion of Na to Na^+ is not favoured energetically, although it may be easier than the ionization of those atoms whose ionization potentials are greater than that of sodium. (2) The combined energy of the two atoms, Na and Cl, is less than the combined energy of the two ions, Na^+ and Cl^- . Therefore the fact that the two atoms acquire electronic configuration of the nearest rare gases after the electron transfer is not sufficient

cause for the process of electron transfer to occur. (3) The formation of the crystal lattice, in which each ion is surrounded by a number of oppositely charged ions, is the principal reason why the sodium and chlorine atoms change to the corresponding ions so readily.

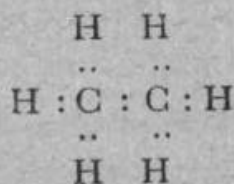
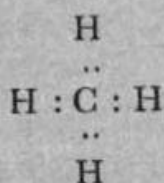
Although the formula of sodium chloride is usually written as NaCl, there is no such thing as a molecule of sodium chloride. Instead the formula NaCl indicates that in a crystal of the salt, there are equal numbers of sodium and chloride ions. Since electrostatic force extends uniformly in all directions, the positive and the negative ions alternate regularly in three dimensions, each sodium ion being surrounded by six chloride ions and each chloride ion being surrounded by six sodium ions. When sodium chloride is dissolved in water, the sodium ions and chloride ions become largely independent and each ion is surrounded by molecules of water. Because the ions are independent and the ionic bond is non-directional, it is meaningless and misleading to write a structural formula for ionic compounds.

COVALENT BOND

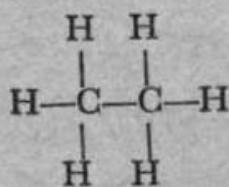
The elements of the groups in the middle of the periodic table, such as boron, carbon and nitrogen, do not form ionic bonds with other atoms. Consider the case of the element carbon from the fourth group of the periodic table. The carbon atom has four electrons in its outer shell (L shell). If it were to form ionic bonds with an element such as chlorine, it would have to lose its four electrons from the L shell and change to C^{4+} which has the electronic configuration of the rare element Helium. The other way to acquire the electronic configuration of a rare gas would be to gain four electrons from an element like sodium and have 8 electrons in its L shell giving rise to the ion C^{4-} . Energy considerations make both of these processes undesirable. The removal of 4 electrons successively from the positively charged carbon nucleus to get C^{4+} would be prohibitively difficult. The formation of C^{4-} will also not be favoured because repulsions between electrons will greatly increase its energy and make it unstable. The carbon atom, therefore generally forms bonds by sharing electrons with other atoms.

In the following compounds the atoms are bonded by shared

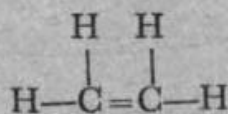
electron pairs, each atom contributing one electron to make the bonding electron pair. Such bonds are called covalent bonds.



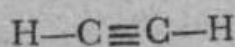
Each of the carbon atoms has a filled L shell of eight electrons and each hydrogen atom has a filled outer shell (K shell) of two electrons. A covalent bond formed by sharing one electron pair is called a *single bond* and is denoted by a short line. There are compounds in which covalent bonds are formed between two atoms by sharing two electron pairs or three electron pairs. A two electron pair bond is called a *double bond* and a three electron pair bond a *triple bond* and they are represented by two short lines and three short lines respectively.



single bond



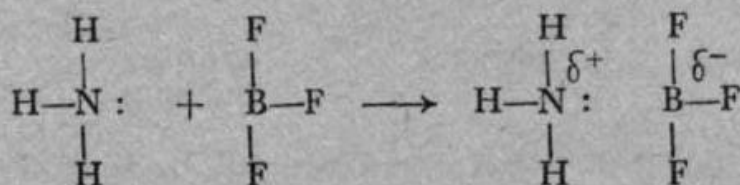
double bond



triple bond

THE COORDINATE COVALENT BOND

In a simple covalent bond each atom contributes one electron to the shared electron pair. There are however, cases in which only one of the two bonded atoms contributes both the shared electrons. A bond formed by sharing an electron pair in which both the electrons are donated by only one atom is called a *co-ordinate covalent bond*. Consider, for example, the reaction of ammonia with boron fluoride :

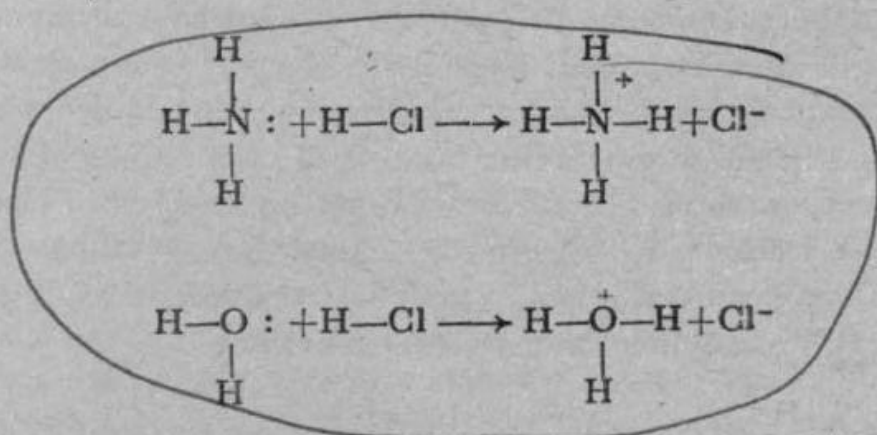


A bond is made between the nitrogen atom and the boron atom and the shared electron pair has been contributed by the nitrogen atom. The electron pair donor atom, nitrogen, acquires a partial positive

charge ($\delta+$), whereas the electron pair acceptor atom, boron, acquires a partial negative charge ($\delta-$) in the final product. Sometimes the co-ordinate bond is represented by an arrow :

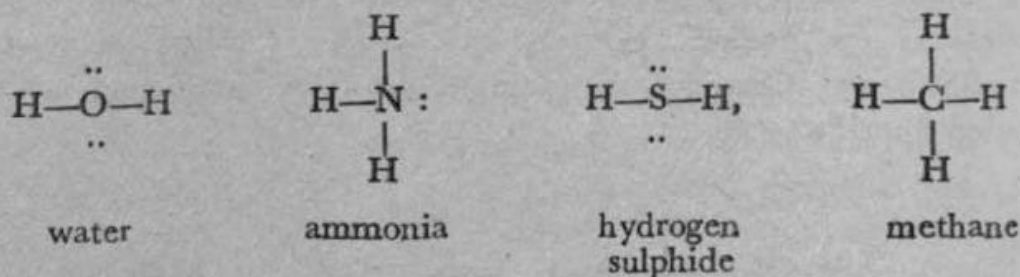


It has associated with itself both covalent and ionic character. A few other examples of coordinate covalent bond are given below :



RECENT INTERPRETATION OF THE COVALENT BOND

The concept that a covalent bond between two atoms consists of a pair of electrons between the two atoms and that each atom contributes one electron to this pair was advanced by an American physical chemist, G. N. Lewis, in 1916. When atoms combine to form molecules by sharing electrons they acquire an inert-gas electron configuration (the Octet Rule). Thus in the following simple molecules each atom has acquired the inert-gas electronic configuration, a shared electron pair being represented by a short line :



These Lewis structures, however, do not tell us what the geometry of the molecule is and why some bonds are weaker than others. It is therefore, necessary to examine the nature of the covalent bond in a little more detail with the help of the modern ideas of the structure of atom.

According to the modern theory electron is believed to have wave properties *e.g.* wave length, frequency, as well as the properties of a particle such as mass, energy, and momentum. Due to this dual nature of electron it is impossible to specify both the position and the momentum ($P=mv$) of an electron at any given instant (*Heisenberg's Uncertainty Principle*). Thus, at any given instant the more accurately it is possible to measure the momentum of an electron, the more uncertain its exact position becomes. It is, therefore, necessary to consider that an electron has only a certain probability of being found at each fixed point in space.

The electrons in an atom surround the positively charged nucleus and are found in energy levels or orbitals. *Orbitals are regions in which the probability of finding the electron is maximum.* An electron in an atom is described by the Schrodinger wave equation which relates the energy of a system to the wave motion. The Schrodinger equation is a differential equation and, therefore, has a large number of possible solutions, because the constants in the equation can have different numerical values. In order to get solutions which are consistent with the experimentally observed behaviour of the electron, the permitted values of these constants are limited and interrelated. Each set of these numbers, called *quantum numbers*, which gives a real solution describes a permissible probability distribution of an electron in the atom. These quantum numbers are briefly discussed below :

(1) *The principal quantum number, n , is a rough measure of the size of an orbital, and determines the distance of an electron from the nucleus. It is a positive integer 1, 2, 3, 4 ... (but not zero). For the shells K, L, M, N, O, etc., the values of n are 1, 2, 3, 4, 5 respectively, i.e., an orbital having $n=1$, will be in K shell and an orbital with $n=3$ will be in M shell and so on. Generally an orbital whose n value is bigger, is larger in size and of higher energy.*

(2) *The azimuthal quantum number, l , determines the shape of an orbital and can have value $=0, 1, 2 \dots (n-1)$, i.e., it is a positive integer but less than n . When*

$l=0$, the orbital is called an s orbital

$l=1$, is a p orbital

$l=2$, is a d orbital

$l=3$, is an f orbital

(3) The magnetic quantum number, m describes the orientation of the orbital in space or the behaviour of an orbital to an applied magnetic field. It can have values $=0, +1, -1, +2, -2$, etc., up to $+l$. For an orbital whose $l=0$, m is also 0. When $l=1$, m is $+1, 0$, and -1 . When $l=2$, $m=+2, +1, 0, -1, -2$ and so on. Thus the values of m pass from $+l$, through 0, to $-l$, i.e.

$$m = +l \longrightarrow 0 \longrightarrow -l$$

(4) The fourth quantum number is the spin quantum number, s , which determines the direction of the spin of an electron. It can have only two values, $+\frac{1}{2}$ and $-\frac{1}{2}$, usually represented as $\uparrow$ and $\downarrow$.

Although for the full description of an electron the values of all the four quantum numbers should be known, the energy of the electron is generally determined by only n and l .

The short notation for specifying an orbital completely is

$$n \ l \ m \ s.$$

For example when $l=0$, the orbital is an s orbital. The value of n for the orbital is written in front of the letter s . Thus if $n=1$, the orbital is the $1s$ orbital. For an orbital whose $l=0$, and $n=2$, the symbol is $2s$. Similarly when $l=1$, and $n=2$, the orbital is a $2p$ orbital.

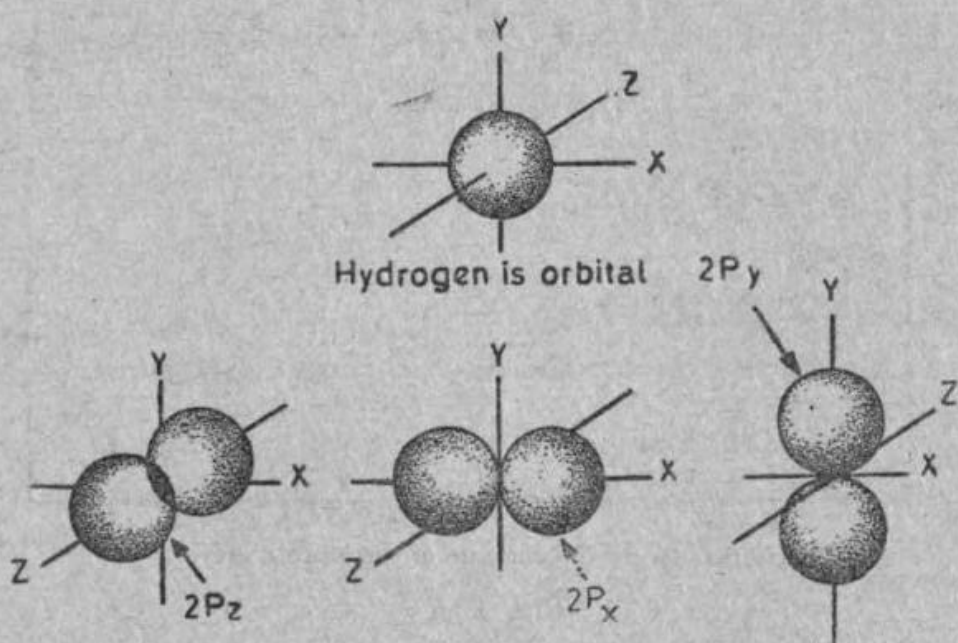
There are three $2p$ orbitals each having $n=2$, and $l=1$ but different values of the magnetic quantum number m ($+1, 0, -1$). Therefore the three $2p$ orbitals are designated as $2p_x, 2p_y$ and $2p_z$. The subscripts x, y and z indicate the orientation of each orbital in space.

Each orbital has a definite amount of energy associated with it. An electron living in the $1s$ orbital can jump into the $2s$ orbital if enough energy is supplied to it. The electron cannot have energy in between the two orbitals. An orbital which surrounds a single atomic nucleus is called an atomic orbital. The $1s, 2s, 2p, 3s, 3p, 3d$, etc., are atomic orbitals.

ORBITALS OF THE HYDROGEN ATOM

The Schrodinger wave equation has been solved only for very simple systems such as the hydrogen atom, which is the simplest system and consists of one proton and one electron.

The orbital of the lowest energy available to the hydrogen electron is the $1s$ orbital. This orbital is closest to the nucleus and is spherically symmetrical. This means that the probability of finding an electron at a given distance r from the nucleus is independent of the direction from the nucleus. The orbital next higher in energy is the $2s$ orbital. It is bigger in size than the $1s$ orbital, but it is also spherically symmetrical around the nucleus. Then there are three $2p$ orbitals which are degenerate which means that they are of equal energies. The $2p$ orbitals are different in shape from the s orbitals. The following figures are representations of the $1s$ and three $2p$ orbitals (Fig. 12.1).



The shapes and orientations of the three $2p$ orbitals of hydrogen atom

Fig. 12.1

It is seen from the above figures that the p orbitals are not spherically symmetrical with respect to the nucleus and that the respective axes passing through the tangent spheres of the three p orbitals are perpendicular to each other.

The $3s$ and $3p$ orbitals are similar in shapes to the $2s$ and $2p$ orbitals but are of higher energies.

The $3d$, $4d$, and $4f$ orbitals have still higher energies and quite different shapes, and are not important for bond making in organic

compounds. A schematic diagram of the various atomic orbitals available to the hydrogen electron is given below (Fig. 12.2).

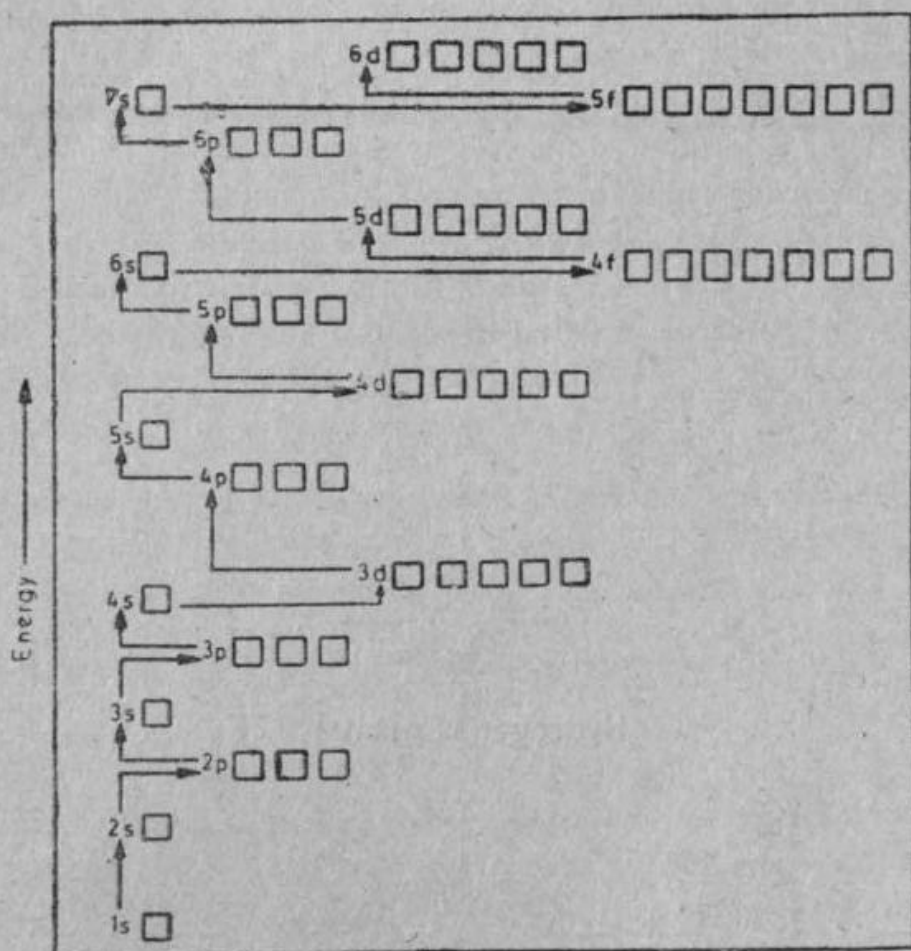


Diagram showing the energies of the atomic orbitals

Fig. 12.2

Since there is only one electron in a hydrogen atom, it will fill the 1s orbital which is closest to the nucleus and of lowest energy if an electron has a number of orbitals available, it will normally live in the most stable orbital or the orbital of the lowest energy.

For building up the electronic configurations of atoms other than hydrogen, it is assumed that the orbitals of other atoms are like the hydrogen-orbitals. These orbitals are filled with electrons successively according to the following rules :

(1) **The Pauli Exclusion Principle:** According to ^{set of} this principle, "no two electrons in the same atom can have the same four quantum numbers." Consider an electron which is occupying a 1s orbital. It means for this electron $n=1$, $l=0$ and $m=0$. Suppose the electron under consideration has $s=+\frac{1}{2}$, which will be indicated by an arrow

($\uparrow$). Now if another electron is put in the same orbital its $n=1$, $l=0$, $m=0$. It can occupy the orbital only if the direction of the spin is opposite to that of the first electron (s must be $-\frac{1}{2}$) symbolized as $\downarrow$. Since there are only two possible values for s , one orbital can contain a maximum of two electrons and only when the direction of the spin of one is opposed to that of the other. Two such electrons which fill the same orbital and have opposite spins are said to be *paired* and are symbolized as $\uparrow\downarrow$. An orbital which is occupied by an electron pair is completely filled. $\downarrow\uparrow$

(2) **Hund's Rule :** When there are available orbitals of equal energy to electrons, the electrons would live in separate orbitals and have the same spin, rather than live in the same orbital and have paired spin. In other words the arrangement $\uparrow \quad \uparrow$ is more stable than the arrangement $\uparrow\downarrow \quad \bigcirc$ provided the two circles represent orbitals of equal energy.

By application of the above rules, the most stable electronic configurations of the atoms of various elements can be built up.

For example, the electronic configurations of hydrogen, helium, carbon, nitrogen, oxygen, neon and chlorine atoms are given below (Fig. 12.3).

H	1 1s
He	$\uparrow\downarrow$ 1s
C	$\uparrow\downarrow \quad \uparrow\downarrow \quad 1 \quad 1$ 1s, 2s, 2p _x , 2p _y , 2p _z
N	$\uparrow\downarrow \quad \uparrow\downarrow \quad 1 \quad 1 \quad 1$ 1s, 2s, 2p _x , 2p _y , 2p _z
O	$\uparrow\downarrow \quad \uparrow\downarrow \quad \uparrow\downarrow \quad 1 \quad 1$ 1s, 2s, 2p _x , 2p _y , 2p _z
Ne	$\uparrow\downarrow \quad \uparrow\downarrow \quad \uparrow\downarrow \quad \uparrow\downarrow \quad \uparrow\downarrow$ 1s, 2s, 2p _x , 2p _y , 2p _z
Cl	$\uparrow\downarrow \quad \uparrow\downarrow \quad \uparrow\downarrow \quad \uparrow\downarrow \quad \uparrow\downarrow \quad \uparrow\downarrow \quad \uparrow\downarrow \quad 1$ 1s, 2s, 2p _x , 2p _y , 2p _z , 3s, 3p _x , 3p _y , 3p _z

Fig. 12.3

The helium and neon atoms (as well as other inert gas atoms) have completely filled orbitals which explains why they are chemically less reactive. Other elements have partially filled atomic orbitals and are chemically reactive. The partially filled orbitals have a single electron in them. A single electron in an orbital is called an *unpaired* electron.

According to the quantum theory, the number of unpaired electrons or the number of partially filled orbitals of the atom of an element is the valence of that element. Thus, hydrogen atom is monovalent, nitrogen atom is trivalent, oxygen atom is divalent and chlorine atom is monovalent. Helium and neon have no unpaired electron and are generally inert. These predictions are essentially in accord with experimental data.

There are a few elements, notably carbon, in which experimental data do not agree to valences predicted by quantum theory, i.e., carbon is tetravalent in most of its compounds, although its atom has only two unpaired electrons and is expected to be divalent. The behaviour of carbon in compound formation will be discussed further.

A covalent bond is formed between two atoms, when the two atoms come so close that a partially filled atomic orbital of one overlaps with a partially filled atomic orbital of the other (when parts of the atomic orbitals of two different atoms occupy the same space, they are said to overlap). The two overlapping atomic orbitals lose their identities and linearly combine to give rise to two new orbitals. These new orbitals encompass both the atomic nuclei. Orbitals which have buried in them two or more atomic nuclei are called molecular orbitals; atomic orbitals surround only one atomic nucleus.

A molecular orbital which is of lower energy (is more stable) than the atomic orbitals from which it was derived, is called a bonding molecular orbital, whereas a molecular orbital which has higher energy (is less stable) than the parent atomic orbitals is called an antibonding molecular orbital.

A σ (Sigma) Bond. *A bonding orbital which is symmetrical about a line joining the two atomic nuclei is called a σ (sigma) orbital. The corresponding antibonding molecular orbital is called a σ^* (sigma star) orbital. These orbitals are filled with available electrons according to the same rules which are applied for filling atomic orbitals.*

Now consider the formation of a hydrogen molecule from two hydrogen atoms. When the two hydrogen atoms come close enough

so that their $1s$ orbitals overlap, the two overlapping orbitals merge to form two molecular orbitals—a σ orbital and a σ^* orbital as pictured below (each *plus* sign stands for a nucleus), Fig. 12.4.

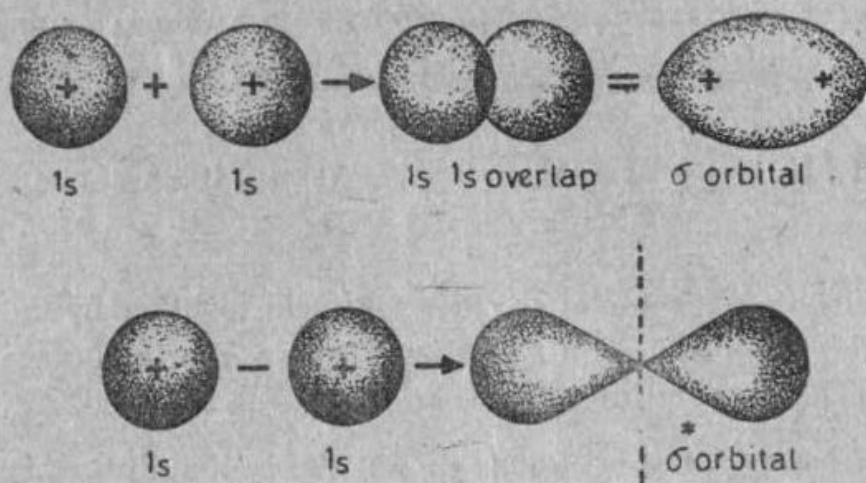


Fig. 12.4

The relative energies of these orbitals are schemetically shown below (Fig. 12.5).

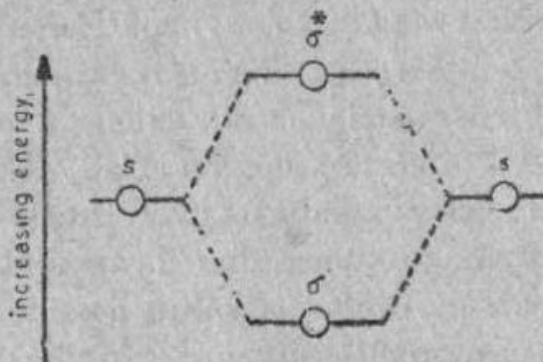


Fig. 12.5

The two available electrons (one from each atom fill the low energy σ orbital and have paired spin ($\downarrow \uparrow$); the high energy σ^* orbital remains empty. In the σ orbital the probability of finding the electron pair is maximum in the region between the two nuclei, *i.e.* the electron cloud is most dense in the region between the two nuclei. Each of the two electrons living in the σ orbital is attracted by both the atomic nuclei. Before the hydrogen molecule was formed each electron was attracted to only one nucleus. The total attractive force of the two nuclei for the two electrons living in the σ orbital of the hydrogen molecule is about twice that of the attractive force when the two electrons lived in two separate atomic orbitals, *i.e.*, when hydrogen was in the atomic state. The increased attraction between nuclei and electrons lowers

the energy of the system (hydrogen molecule) and the lowering in energy more than compensates the energy increase due to nucleus-nucleus repulsions and electron-electron repulsions. Thus 103 kcal. mole⁻¹ of energy is released when two hydrogen atoms combine to form a hydrogen molecule. 103 kcal. mole⁻¹ is called the *bond energy* of H—H bond.



The two atomic nuclei are therefore held together by the electron pair in the σ orbital. The two electrons in a σ orbital are called σ electrons and the resulting bond is referred to as a σ bond.

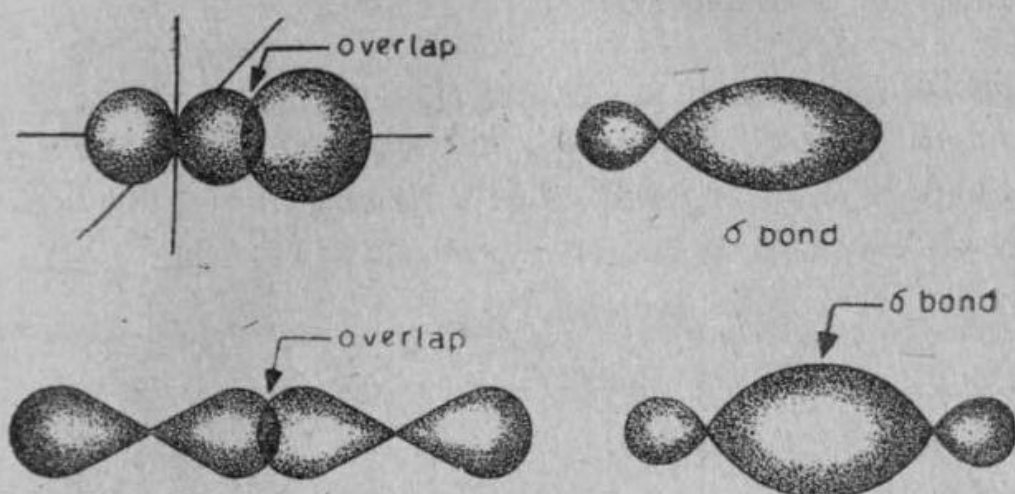
In a non-bonding orbital (e.g., σ^*) the probability of finding the electrons is *minimum* in the region between the nuclei. Thus if an antibonding orbital is filled with electrons it will make the molecule unstable, because nucleus-nucleus repulsions are maximized in the absence of electron density between the nuclei.

A molecular orbital would be more stable if there is greater overlap between the atomic orbitals from which it is formed. In the ideal state the two nuclei will have maximum attraction for the two electrons if the two overlapping orbitals are superimposed. This would, however, increase the nucleus-nucleus repulsions to an extent which would more than offset the advantage gained due to maximized nuclei-electron attractions. To create an orbital of lowest possible energy the nuclei are, therefore, at a compromise distance. In the hydrogen molecule this balance is reached when the distance between the two nuclei is 0.74 Å. This distance is called the *bond length*.

From the above discussion it is obvious why a two electron covalent bond is specially stable. If there are three or four electrons available, the extra electrons will have to be put in the high energy σ^* orbital (Pauli Exclusion Principle), which will make the system unstable. Similarly a single electron in σ bond, electron in the σ orbital, will not be as strong as a two electron σ bond because the electron-nuclei attractive forces in the former case will be relatively weaker.

A σ bond is also formed between two atoms when a p orbital of one atom overlaps with an s orbital of the other atom (s - p overlap) or when a p orbital of one atom overlaps with a p orbital of the other, provided the two overlapping orbitals approach each other in such a way that the

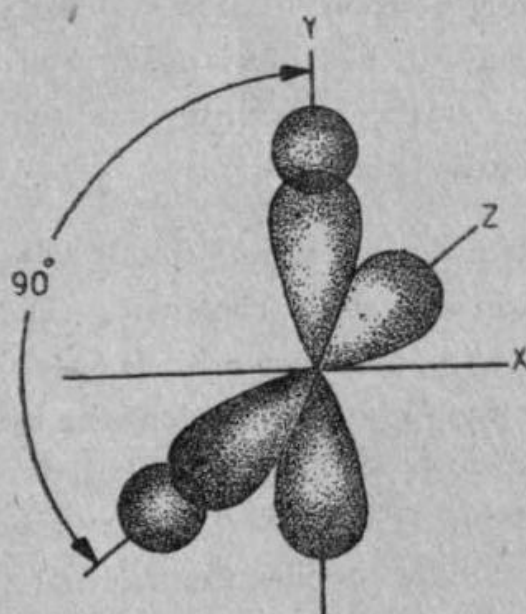
axes of the two atomic orbitals that have overlapped form one single straight line (Fig. 12.6).



- (a) overlap of a hydrogen $1s$ orbital with a $2p$ orbital
 (b) overlap of a $2p$ orbital with another $2p$ orbital

Fig. 12.6

In the formation of a molecule of water (H—O—H) from an oxygen atom and two hydrogen atoms, the two partially filled $2p$ orbitals of oxygen overlap with two hydrogen $1s$ orbitals creating two σ bonds between the oxygen atom and the two hydrogen atoms. (Fig. 12.7).



overlap of hydrogen $1s$ orbitals with $2p_y$ and $2p_z$ orbitals
 centered on an oxygen atom

Fig. 12.7

Because the axes of the two $2p$ orbitals are perpendicular to each other the H—O—H bond angle is expected to be 90° , which is near the experimentally determined bond angle.

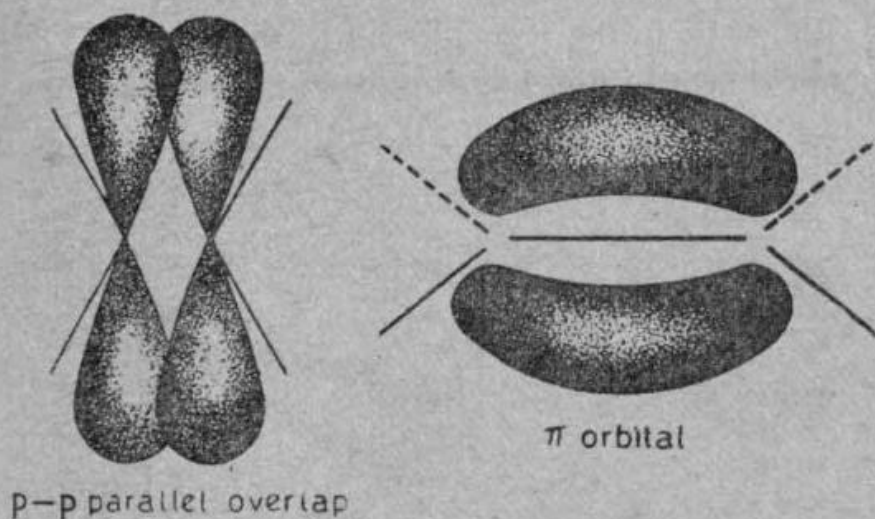
Similarly, a molecule of ammonia is formed by the overlap of the three partially filled $2p$ orbitals of the nitrogen atom with three hydrogen $1s$ orbitals. Since the $2p$ orbitals are perpendicular to each other, the H—N—H bond angles in NH_3 are expected to be 90° each.

A co-ordinate covalent bond is formed by the overlap of a completely filled orbital of the donor atom with an empty orbital of the acceptor atom. The two electrons which fill the resulting orbital are, thus, both contributed by the donor atom.

A π (Pi) Bond. Besides the σ bond, another type of bond can also exist between two atoms. If the p orbital of one atom has its axis parallel to that of the p orbital of another atom, and if these two p orbitals overlap, two new molecular orbitals are formed whose shapes are different from the σ and σ^* orbitals. The bonding molecular orbital is called a π (π) orbital, whereas the antibonding molecular orbital is called π^* (π star) orbital. The π orbital has two regions of electron density above and below the nuclei, instead of a single region of electron density as in a σ orbital. The two electrons from the two overlapping p orbitals fill the low energy π orbital (π^* , π star remains empty) and are called π electrons. The resultant bond is called a π bond.

It should be realised that the two p orbitals whose axes are parallel must have their axes in one plane (coplanar). The overlap is not as effective as a σ overlap, i.e., when two orbitals overlap so that their axes make a single straight line (σ bond formation) the overlap is more complete than when the two overlapping orbitals have their axes parallel to each other (π overlap). This is why, whenever possible, the orbitals will overlap in the σ manner to allow the maximum overlap of atomic orbitals. A π bond is only formed when two overlapping p orbitals are on two atoms which are already bonded. Two such p orbitals give a maximum overlap when their axes are parallel, although this overlap is not as good

as a σ overlap between two p orbitals. The following is a representation of a π bond formation. (Fig. 12.8).

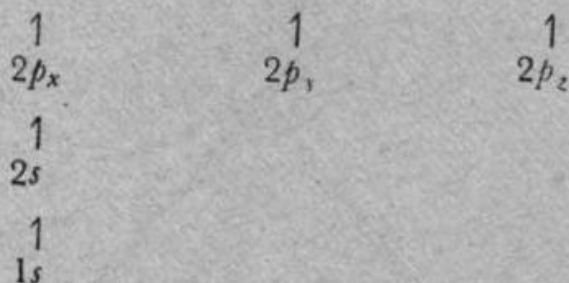


The $\sigma \pi$ formulation of ethylene

Fig. 12.8

VALENCE OF CARBON

Orbital Hybridization : Although the most stable electronic configuration of a carbon atom (having two partially filled $2p$ orbitals) requires it to be divalent, carbon is tetravalent in the majority of its compounds. In order to explain this seeming anomaly, it is assumed that an electron from the $2s$ orbital is promoted to an empty $2p$ orbital, giving the electronic configuration :



electronic configuration of carbon atom after
promotion of a $2s$ electron to $2p$

It is then imagined that the $2s$ and the three $2p$ orbitals are mixed to get four equivalent orbitals. $2s + 2p_x + 2p_y + 2p_z = 4sp^3$.

The resultant hybrid orbitals are called sp^3 orbitals and the process of combining the s and the three p orbitals to get four sp^3 hybrid orbitals is called sp^3 hybridization. The symbol sp^3 signifies that each sp^3 orbital

is made up of s and p orbitals in the ratio of 1 : 3. The sp^3 orbitals are directed from the centre of a regular tetrahedron to its four corners. They are thus oriented at angles of 109.5° with each other. The four sp^3 orbitals do not lie in the same plane, *i.e.*, they are not coplanar and have the shape shown in Fig. 12.9.

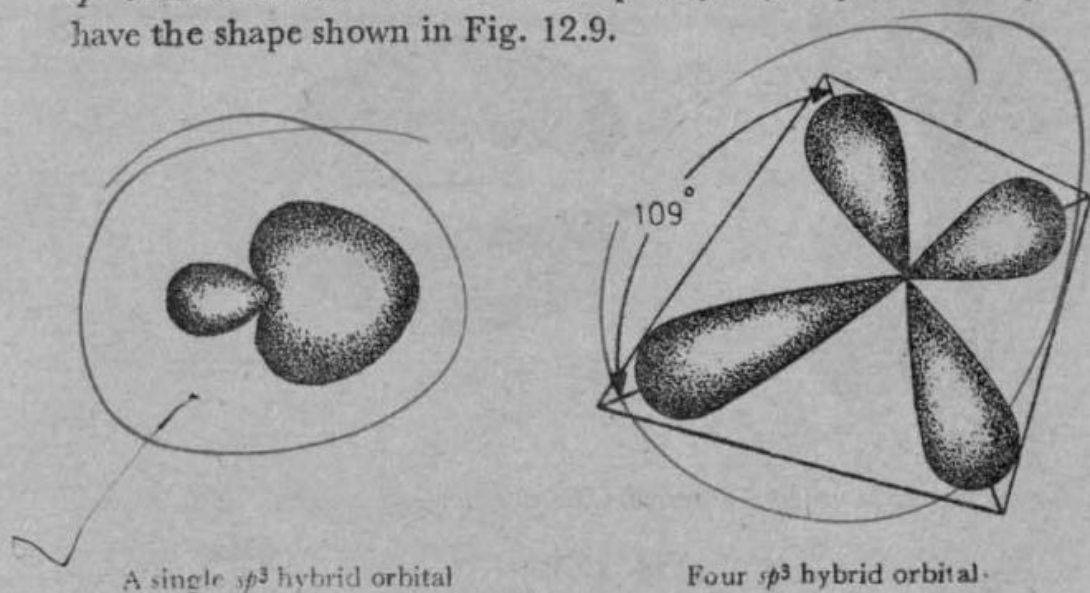


Fig. 12.9

When the four carbon sp^3 orbitals overlap with, for example, the $1s$ orbitals of four hydrogen atoms, a molecule of methane (CH_4) is formed, in which there are four σ bonds (each due to sp^3-s overlap) and each $\text{H}-\text{C}-\text{H}$ bond angle $= 109.5^\circ$ (tetrahedral), Fig. 12.10.

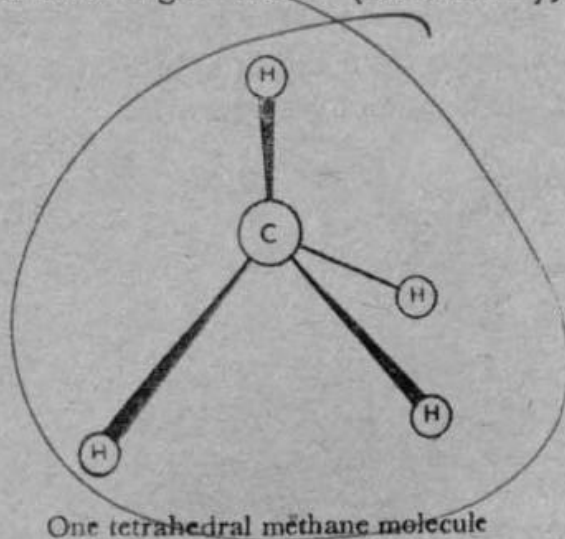
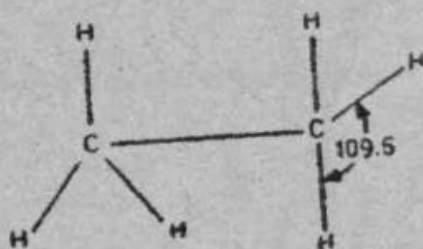


Fig. 12.10

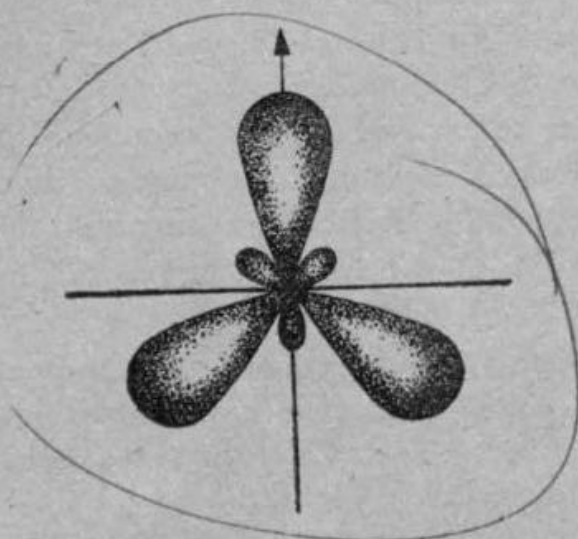
The promotion of an electron from the $2s$ to a $2p$ orbital costs energy $= 161.5 \text{ kcal mole}^{-1}$. But by doing this carbon forms a total of four covalent bonds instead of two which it would have formed if it had used its two partially filled $2p$ orbitals. The formation of two

additional bonds releases $186 \text{ kcal mole}^{-1}$ energy, thus, more than compensating the expenditure of $161.5 \text{ kcal mole}^{-1}$ for electron promotion. A molecule of ethane has seven σ bonds as shown below :



The C-H bonds result from the sp^3-s overlap and C-C bond results from sp^3-sp^3 overlap. All H-C-H bond angles are 109.5° .

The sp^3 hybridization occurs when carbon is bound to four other atoms. When it is bound to only three atoms, the $2s$ and two of the three $2p$ orbitals are hybridized to get three equivalent sp^2 hybrid orbitals (sp^2 orbitals are composed of s and p orbitals in a ratio of 1:2). These three sp^2 orbitals lie in the same plane and at 120° angles (Fig. 12.11).



The three sp^2 orbitals

Fig. 12.11

The remaining unhybridized p orbital is perpendicular to the plane of the three sp^2 orbitals. Thus in ethylene each carbon atom is joined to two hydrogen atoms by σ bonds formed by the overlap of one of the sp^2 orbitals on carbon and the $1s$ orbital of hydrogen. There is also a σ bond between the two carbon atoms which is the result of sp^2-sp^2 overlap. These σ bonds (represented by short lines) and the

unhybridized p orbitals of the two carbons are shown in Fig. 12.12.

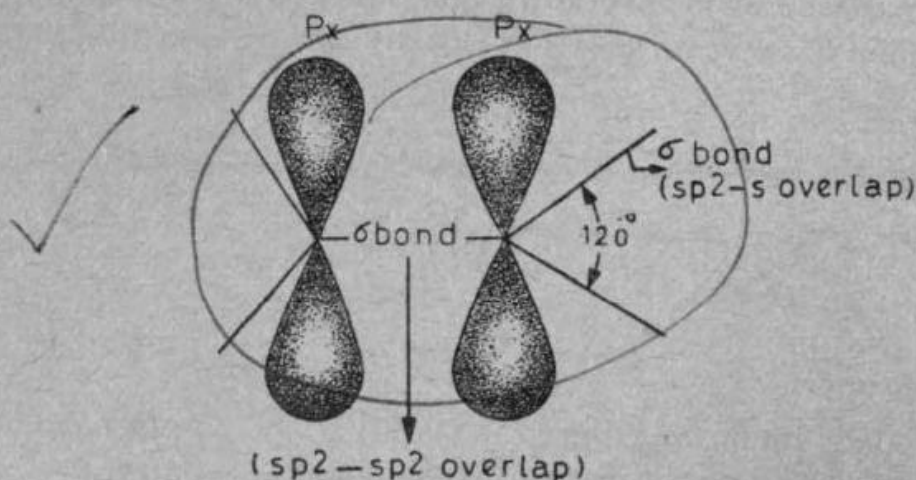
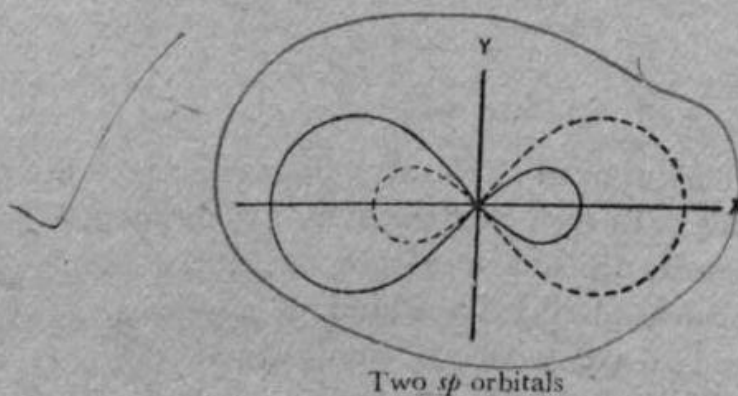


Fig. 12.12

The two unhybridized p orbitals are perpendicular to the axis joining the two carbon nuclei and their axes are parallel. In ethylene they are near enough to overlap and form a π molecular orbital and a π^* orbital. The electrons fill the π orbital leaving the high energy antibonding π^* orbital empty. There are, thus, two different bonding molecular orbitals between carbon atoms. If these are filled with electrons two different kinds of bonds result, a σ bond and a π bond. The π bond is more diffused and the weaker of the two. The electrons in the π bond are more exposed to the environment than those of the σ bond. For these reasons π electrons are more easily attacked by other reagents as compared with σ electrons, being held more tightly by the nuclei. Compounds with π bonds are, in general, more reactive than compounds with σ bonds only.

When carbon atoms are attached to two other atoms, they hybridize one $2s$ and one $2p$ orbital to give two sp hybrid orbitals leaving two $2p$ orbitals as unhybridized. The axes of the two sp orbitals form a single straight line (they are coaxial), Fig. 12.13.



Two sp orbitals

Fig. 12.13

In the acetylene, $\text{H}-\text{C}\equiv\text{C}-\text{H}$, the two $\text{C}-\text{H}$ bonds result from $sp-s$ overlap in σ fashion, whereas a $\text{C}-\text{C}$ bond is formed by the σ overlap of the sp orbital of one carbon with the sp orbital of the other carbon (Fig. 12.15).

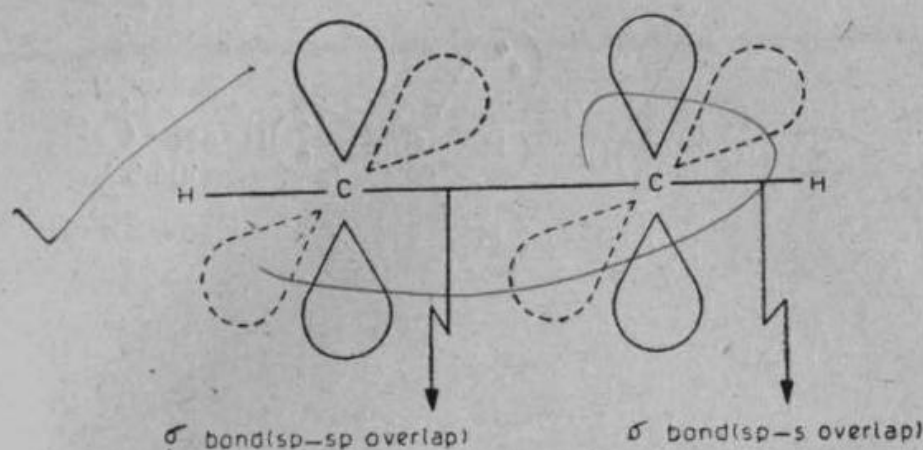


Fig. 12.15

The residual two $2p$ orbitals of one carbon atom overlap with the two $2p$ orbitals of the other carbon atom, forming two π bonds. Thus in acetylene there is one σ bond and two π bonds between the two carbon atoms (Fig. 12.16).

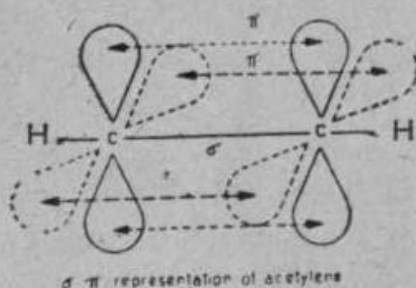


Fig. 12.16

The observed bond angles in $\text{H}-\text{O}-\text{H}$ and NH_3 are 104.5° and 107° respectively which are nearer to the value 109.5° rather than to 90° predicted if oxygen and nitrogen atoms are assumed to use their partially filled p orbitals, as discussed earlier. An improved treatment might be that in which the oxygen atom in H_2O and the nitrogen atom in NH_3 hybridize their $2s$ and three $2p$ orbitals to generate four sp^3 hybrid orbitals. In water the two $\text{O}-\text{H}$ σ bonds would result from sp^3-s overlap and the two remaining sp^3 orbitals will contain a pair of electrons each. Similarly in NH_3 the three $\text{N}-\text{H}$ σ bonds will be formed due to sp^3-s overlap and the remaining sp^3

orbital will be filled with a pair of electrons. Thus both water and NH_3 will have tetrahedral geometry like the molecule of methane (Fig. 12.17).

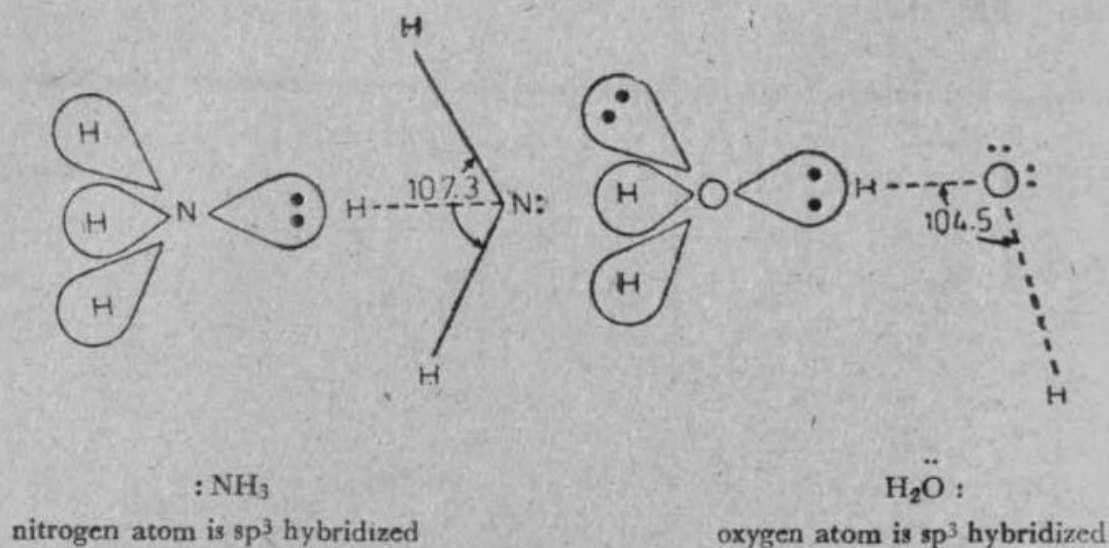
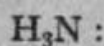
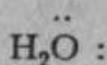


Fig. 12.17

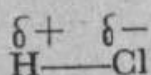
The oxygen atom in water has two electron pairs in two sp^3 orbitals which are not used in bond making and the nitrogen atom in NH_3 has one such electron pair. These are called unshared electron pairs and are represented by two dots each in simple structural formulas :



The above discussion shows how the molecular orbital approach leads to the prediction of bond angles (geometry) of a molecule. It also shows that unlike an ionic bond which is equally strong in all directions, the covalent bond is a *directed* bond. Furthermore σ bonds may be formed by overlapping different types of atomic orbitals (e.g., $s-s$, $s-p$, $p-p$, sp^3-sp^3 , sp^2-sp^2 , sp^2-sp^3 , sp^3-s , sp^2-s overlaps). Because the overlapping abilities of these orbitals are different, one σ bond may be stronger than another σ bond.

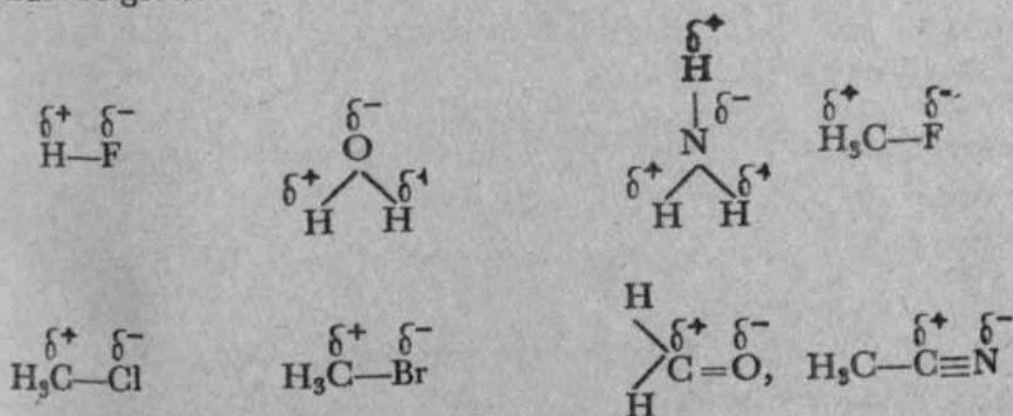
Ionic Character of Covalent Bonds : In the hydrogen molecule the two nuclei buried in the σ orbital are identical and therefore these exert equal attraction on the electron cloud between them. The same is true for a chlorine molecule ($\text{Cl}-\text{Cl}$), or a bromine molecule ($\text{Br}-\text{Br}$). However, when the two nuclei inside a molecular orbital are not identical, the electrons are not shared equally by the two unlike nuclei. Consider, for example, the $\text{H}-\text{Cl}$ molecule.

The nucleus of chlorine has more positively charged protons in it than the nucleus of hydrogen gas. The result is that the negatively charged electron pair in the σ orbital will not be equally attracted by the two nuclei. Rather the electron cloud will be more dense near the chlorine nucleus relative to the less positive hydrogen nucleus. The chlorine atom is said to be more electronegative than the hydrogen atom, which means that the total attraction of the chlorine nucleus for electrons is greater than the total attraction of the hydrogen nucleus for electrons. Thus in the H—Cl molecule, there will be a partial positive charge on hydrogen and a partial negative charge on chlorine as shown.

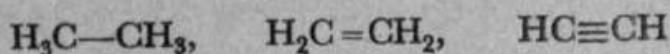


The covalent bond between H and Cl is called a *partially ionic* covalent bond. Because one of its ends is relatively negative while the other is relatively positive, that is, because there is a negative pole and a positive pole, it is said to be *polarized* and sometime given the name "*polar bond*".

Covalent bonds are partially ionic if they exist between two unlike atoms, which have different electronegativities. The ionic character of a bond increases with the increase in the difference of electronegativities between the two bonded atoms. A few examples of partially ionic bonds are given below :



The following bonds are not ionic in character :

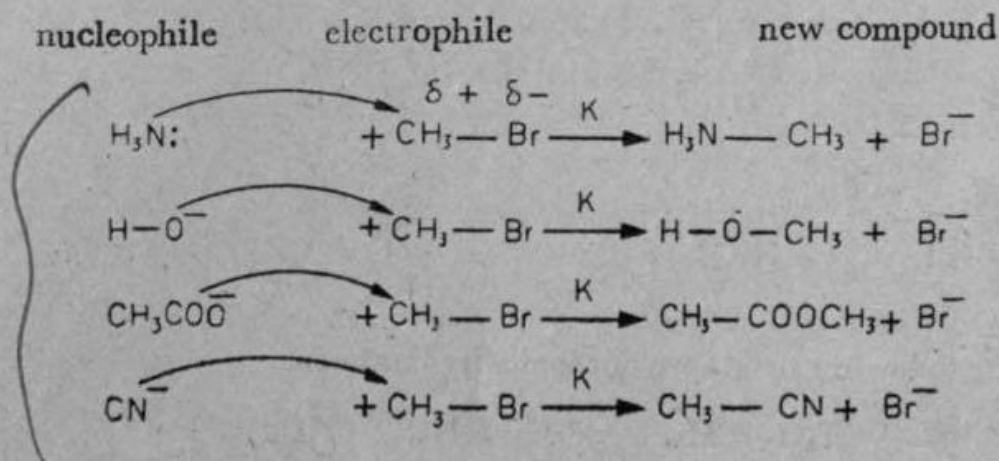


Both physical and chemical properties of organic compounds are determined to a large extent by the ionic character of the bonds in the molecules.

The polarity of a bond will tell what kind of reaction can occur at that bond. Further a partially ionic bond can make a molecule polar and thus affect its melting point, boiling point, and solubility :

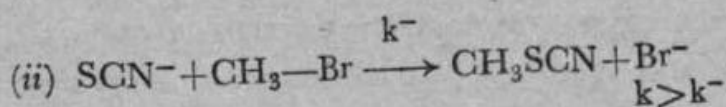
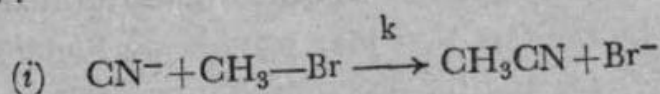
Electrophiles (or acids) : When in an organic compound, such as $\overset{\delta+}{\text{H}_3\text{C}}-\overset{\delta-}{\text{Cl}}$, the carbon atom is bonded to a more electronegative atom like the chlorine atom, the C—Cl bond is partially ionic, with a partial positive charge on carbon. Such a carbon atom which is deficient in electrons and can, therefore, accept available electrons, from some other atom, is said to be *electrophilic* (electron-loving) in nature. *The compounds or species which are deficit in electrons or have tendency to accept a pair of electrons to make a new covalent bond are called electrophile (electron-loving).* Similarly the hydrogen atom in $\overset{\delta+}{\text{H}}-\overset{\delta-}{\text{Cl}}$ and the carbon atom in $\overset{\delta+}{\text{H}_2\text{C}}=\overset{\delta-}{\text{O}}$ are electrophiles or electrophilic in nature.

The compounds or species which have a tendency to donate a pair of electrons to an electrophile to make a new covalent bond are called nucleophiles (nucleus-loving). For example, the anions OH^- , CH_3COO^- , I^- , Br^- and CN^- are nucleophilic in nature. $\ddot{\text{N}}\text{H}_3$ and $\text{H}_2\ddot{\text{O}}$, which have unshared electron pairs, are also nucleophiles. Compounds having a double bond (a σ and a π bond) between two carbon atoms as represented by two short lines, $>\text{C}=\text{C}<$, also act as nucleophiles because the double bond can donate the π electrons to an electrophile. Examples of new bond formation between nucleophiles and electrophiles are given below :

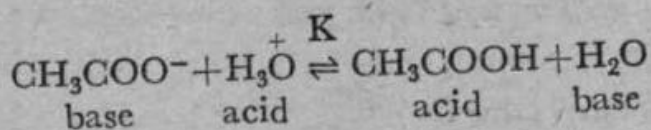
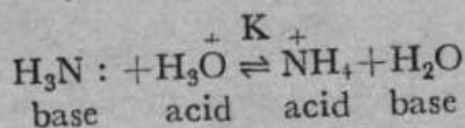


A curved arrow in these equations signifies that a pair of electrons is donated by the nucleophilic atom to the electrophilic atom to make a new covalent bond.

The reactions of nucleophiles with compounds containing an electrophilic carbon atom are usually slow and their rates can be measured. If, for example, the rates of the reaction of $\text{CH}_3\text{—Br}$ are determined separately with a given number of nucleophiles in hydroxylic solvents (*e.g.*, acetone-water mixture in each case), the rate of reaction will be different with different nucleophiles. The nucleophile whose rate is faster (the rate constant, k , is larger) is said to be a stronger nucleophile. The observed order of nucleophilic reactivity towards electrophilic carbon is usually $\text{CN}^- > \text{I}^- > \text{SCN}^- > \text{Br}^- > \text{Cl}^- > \text{F}^-$, *i.e.*, for the reactions :



Acids and Bases : Bases are also defined as species which have a tendency to donate a pair of electrons to form a new covalent bond. Thus all the nucleophiles mentioned above may also be called bases. The term “base” is usually used when the electron pair is donated to an electron deficient hydrogen atom. For example the following reactions will be called acid-base reactions instead of nucleophile-electrophile reactions :



Acid-base reactions are generally rapid and reversible and involve transfer of a proton from one species to other. If the equilibrium constants, K , are determined for the above reactions, that base will be said to be stronger which has larger K .

In short bond formation between an electron pair donor atom and an electron pair acceptor atom will be called a nucleophile electrophile reaction if the electron pair acceptor atom is a carbon atom. Similar reactions will be called acid-base reactions if the electron pair acceptor atom is a hydrogen atom. The OH^- , $\text{C}_2\text{H}_5\text{O}^-$, $(\text{CH}_2)_3\text{N}:$, CO_3^{2-} are examples of strong bases.

A majority of organic reactions are simply a result of the combination of a nucleophile with an electrophile. The characteristic properties of the various functional groups usually stem from the fact that the functional group has either a nucleophilic centre or an electrophilic centre. Those compounds which have no functional group in the molecule are usually unreactive. For example, compounds of carbon and hydrogen (hydrocarbons), which have only single covalent bond in the molecule are chemically unreactive. The whole family of these hydrocarbons, called the saturated hydrocarbons, is characterized by the fact that they contain no functional group and consequently no nucleophilic or electrophilic atom in the molecule. They are, therefore, unreactive towards reagents like aqueous acids, alkalis and solutions of potassium permanganate which usually react in ionic form.

Questions

1. Chemical reactions in general involve the breaking of old bonds and the making of new ones. Describe the three possible ways in which a covalent bond $A : B$ may be broken.
2. How do you justify the statement "Carbon does not form ionic bonds"?
3. How does a covalent bond differ from a co-ordinate covalent bond? Discuss the bonding in the following compounds :
 - (a) ammonium hydroxide,
 - (b) methyl alcohol, and
 - (c) dimethyl ether.
4. What limitations do Pauli Exclusion Principle and Hund's Rule impose upon the build up of electrons in orbitals?
5. Describe a simple rule to predict the valence of the following atoms (atomic numbers are given within brackets) :
 - (a) Na (11), (b) He(2), (c) O(8), (d) C(6), and (e) S (16).
 Why is the rule disregarded in case of carbon?
6. Define the following terms :
 - (a) bond energy,
 - (b) an orbital,
 - (c) unpaired electrons,
 - (d) bond length.

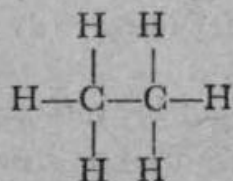
7. Differentiate clearly between :
 - (a) a bonding and an antibonding orbital,
 - (b) ionic and a polar bond,
 - (c) sigma and pi bond,
 - (d) atomic and a molecular orbital, and
 - (e) pure and hybridized orbital.
 8. Draw the atomic orbital picture of the following compounds :
 - (a) methane,
 - (b) hydrogen sulphide,
 - (c) methyl amine.
 9. Describe three principal ways of carbon orbital hybridization. How does molecular orbital approach help us in predicting the geometry of ethane, ethene and ethyne molecules?
 10. Using positions in the periodic table as a criterion of electronegativity, classify the following substances as ionic or covalent :
 - (a) NaCl, (b) Cl_2 , (c) CH_4 , (d) CO_2 and (e) $\text{CH}_3\text{—Cl}$.
 11. Which bonds in the following molecules are polar? (Indicate the direction of polarity by an arrow, $\longrightarrow$, over the covalent bond, the head of the arrow representing the negative end)?
 - (a) H_2O , (b) CH_3Br , (c) CH_3OH , (d) CO_2 and (e) HCl .
 12. Which of the following compounds behave as electrophiles and which as nucleophiles. Indicate the electrophilic or nucleophilic centre by partial ionic charges?
 - (a) ethene,
 - (b) methyl iodide,
 - (c) ammonia,
 - (d) sodium cyanide,
 - (e) methyl alcohol,
 - (f) aluminium bromide,
 - (g) HCl ,
 - (h) silver nitrite,
 - (i) water.
-

CHAPTER 13

HYDROCARBONS

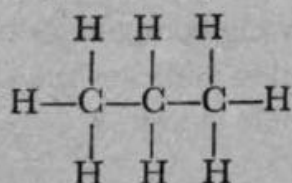
General Framework : Hydrocarbons, as the name signifies, are compounds containing carbon and hydrogen atoms only. We are all familiar with "Sui gas" which consists largely of *methane*, the simplest hydrocarbon known. It has the molecular formula CH_4 . Methane is an example of a saturated hydrocarbon, because all the four available valences of carbon have been fully utilized. Hydro-carbons, such as methane, are known as *alkanes*, or more commonly as *paraffins*.

Carbon is unique in that it can combine with itself in a variety of ways to form chains and rings. Let us try to construct these *chains* of carbon starting with two carbon atoms. Obviously only one arrangement is possible for a molecule having two carbon atoms, as shown :

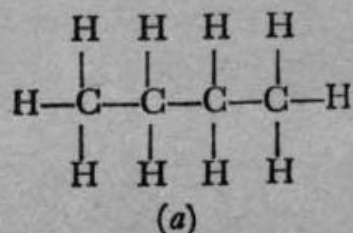


The hydrocarbon with two carbon atoms is called ethane.

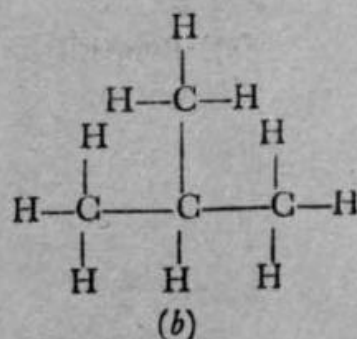
Three carbon atoms may similarly be linked to form the molecule



commonly referred to as *propane* (C_3H_8). As is obvious from the structural formula, only one skeletal arrangement (as shown above) is possible for propane. Incorporation of the fourth carbon could, obviously, take place at *two* different points either at one of the $-\text{CH}_3$ carbon or at the central $-\text{CH}_2-$ carbon. The shape of C_4H_{10} molecule would then become :



or



Structures of two Butanes : The butane (a) is a logical continuation of the propane chain in a straight manner making the molecule as one continuous stem, and is called normal-butane or simply *n*-butane. (The prefix normal or *n*-indicates that the compound has straight chain of carbon atoms). The butane with structure (b) has a three carbon stem with the fourth carbon branching out at the middle. This is referred to as *iso*-butane. (The prefix *iso*-indicates that the carbon chain is branched). The *n*-butane and *iso*-butane have the same molecular formula (C_4H_{10}) but different skeletal arrangement of carbon atoms ; *n*-butane and *iso*-butane are isomers of one another, and the phenomenon is known as *isomerism*. Isomerism is not possible with propane because propane evolves from ethane which is built up of two identical units *i.e.* (H_3C-CH_3), and hence only one arrangement is possible for C_3H_8 hydrocarbon. Isomerism becomes possible with C_4H_{10} hydrocarbon, because its precursor, propane, has two types of carbons : two identical $-CH_3$ groups flanking a central $-CH_2-$ carbon, and hence the fourth carbon could attach itself at either point thereby giving rise to the two butanes.

As we go on building the chain, the number of possible isomers increases. Thus on constructing C_5 hydrocarbons from the two butanes, the pentanes (C_5H_{12}) would look somewhat like the following Fig. (13.1) :

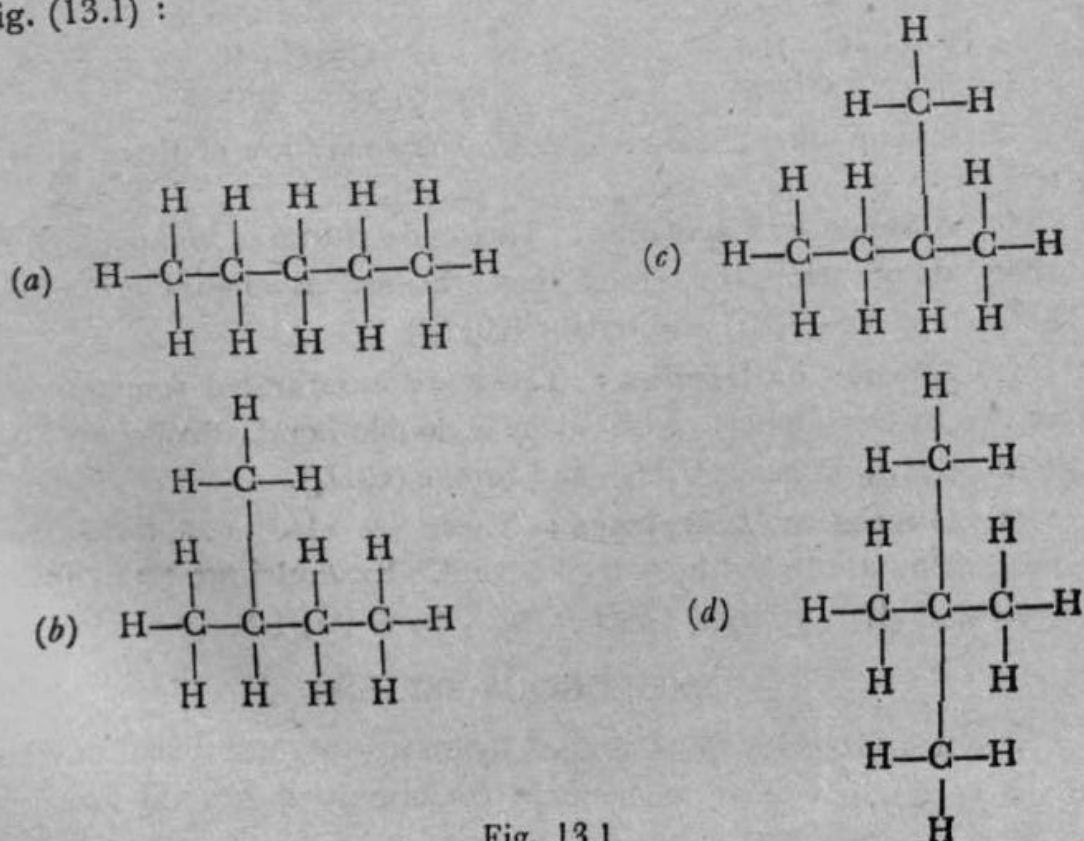


Fig. 13.1

STRUCTURES OF ISOMERIC PENTANES

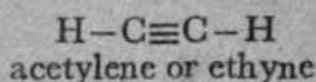
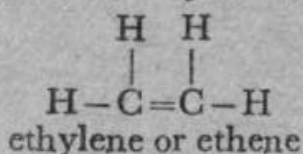
Structure (a) has a continuous carbon chain and hence is the *n-pentane*. Structures (b) and (c) are branched, but are identical and they constitute the *iso-pentane*. The (d) isomer is also branched, but the pattern is different from that of *iso-pentane* and hence constitutes a third isomer, commonly known as *neo-pentane*.

Thus, it is seen that as the number of carbon atoms increases the number of patterns into which these could be arranged also increases. Only one ethane or propane is possible, but two isomeric butanes and three isomeric pentanes exist.

One could similarly construct five isomeric hexanes (C_6H_{14}) and eight isomeric heptanes (C_7H_{16}). We thus find that linking of carbon atoms could result in the formation of either straight chains or branched chains of different shapes and sizes. This built up is primarily responsible for the incredibly large number of carbon compounds.

UNSATURATED HYDROCARBONS

In contrast to the saturated hydrocarbons, we have another class of compounds termed as *unsaturated hydrocarbons*. These are compounds in which two of the carbon atoms are joined by a double or a triple bond. *Ethylene* and *acetylene* are typical examples of the two types :



To sum up, then, open chain hydrocarbons are of three distinct types :—

(a) **Alkanes or Paraffins** : These are saturated compounds, the carbon atoms being linked by single bonds. Examples are ethane (C_2H_6), propane (C_3H_8) and butane (C_4H_{10}).

(b) **Alkenes or Olefins** : These are unsaturated compounds in that two carbon atoms are linked by a double bond. Examples are : ethene (C_2H_4), propene (C_3H_6), and butene (C_4H_8).

(c) **Alkynes or Acetylenes** : These are also unsaturated, two carbon atoms are linked by a triple bond. Examples are : ethyne or acetylene (C_2H_2), propyne (C_3H_4), and butyne (C_4H_6).

HOMOLOGOUS SERIES

A quick glance at the saturated hydrocarbons, mentioned earlier, would reveal that these compounds conform to a general formula,

C_nH_{2n+2} , where n is the number of carbon atoms in the molecule. In building up the hydrocarbon chains we started with the simplest compound methane and proceeded to add one saturated carbon, with its associated hydrogen atoms, at a time. Since each saturated carbon brings with it two hydrogen atoms, this process results in the addition of $-CH_2$ (i.e., a methylene group) to the molecular formula, at each stage. A set of similar compounds differing from each other by an integral number of CH_2 groups is called a homologous series.

Each member of a homologous series tends to react like the other member of that series. Hence the principle of *homology* is a valuable aid in understanding the physical and chemical behaviour of a compound. The principal effect of increasing molecular weight in a homologous series is a smooth gradation in the physical properties of the compounds. Melting and boiling points tend to increase with increasing molecular weight in a homologous series. This tendency is illustrated by the following data (Table 13.1) :

Table 13.1

PHYSICAL PROPERTIES OF SOME ALKANES,
ALKENES AND ALKYNES

Compound	M.P. ($^{\circ}C$)	B.P. ($^{\circ}C$)
<i>Alkanes :</i>		
Ethane (C_2H_6)	-183	-89
Propane (C_3H_8)	-188	-42
<i>n</i> -butane (C_4H_{10})	-138	-1
<i>n</i> -pentane (C_5H_{12})	-130	36
<i>Alkenes :</i>		
Ethene (C_2H_4)	-169	-104
Propene (C_3H_6)	-185	-48
1-butene (C_4H_8)	-185	-6
1-pentene (C_5H_{10})	-165	30
<i>Alkynes :</i>		
Ethyne (C_2H_2)	...	-84
Propyne (C_3H_4)	-103	-23
1-butyne (C_4H_6)	-126	9
1-pentyne (C_5H_8)	-106	40

The distinguishing features of a homologous series may be summarized as follows :

- (i) All members of a homologous series have similar structure. Thus all saturated hydrocarbons are open chain compounds in which all carbon to carbon bonds are single bonds.
- (ii) Physical properties of homologues change progressively, and more or less regularly, with the number of carbon atoms.
- (iii) Members of a homologous series can be prepared by methods applicable to a particular member (commonly referred to as general methods).
- (iv) Members of a homologous series have almost similar chemical properties.
- (v) The composition of all members of a homologous series can be expressed by a general formula. C_nH_{2n+2} , C_nH_{2n} , and C_nH_{2n-2} represent the general formulas of alkanes, alkenes and alkynes respectively.
- (vi) Successive members always differ in composition by CH_2 (and in molecular weight by 14). Any two members of a series, therefore, differ by some multiple of CH_2 .

Importance of homology in organic chemistry can hardly be over-estimated. As a result of this large number of organic compounds can be studied as families rather than as individuals. This eliminates much detailed description and makes it possible to concentrate on structural features which are responsible for common properties.

NOMENCLATURE

We have seen earlier that the number of known organic compounds is extremely large and many more are prepared in the laboratory each year. As such it is all the more important that some systematic method of naming organic compounds be evolved. The saturated hydrocarbons are the simplest of organic compounds and are relatively unreactive. Hence they form a logical basis for a systematic method of nomenclature. The names of normal saturated hydrocarbons upto C_{10} are given in table 13.2.

Table 13.2

BASIC NAMES OF SATURATED HYDROCARBONS

C_1 methane
 C_2 ethane
 C_3 propane
 C_4 butane
 C_5 pentane

C_6 hexane
 C_7 heptane
 C_8 octane
 C_9 nonane
 C_{10} decane

These names are the basic tools of nomenclature. It is clear that all names end in *-ane* as does the family name *alkane*.

The second important basis of nomenclature is the *radical*. Thus ethane molecule is formed by substituting one hydrogen atom of methane with one —CH_3 group, called a *methyl* radical. Similarly propane is formed by substituting one hydrogen atom of ethane with one methyl radical. The process may be picturised as follows (Fig. 13.2) :

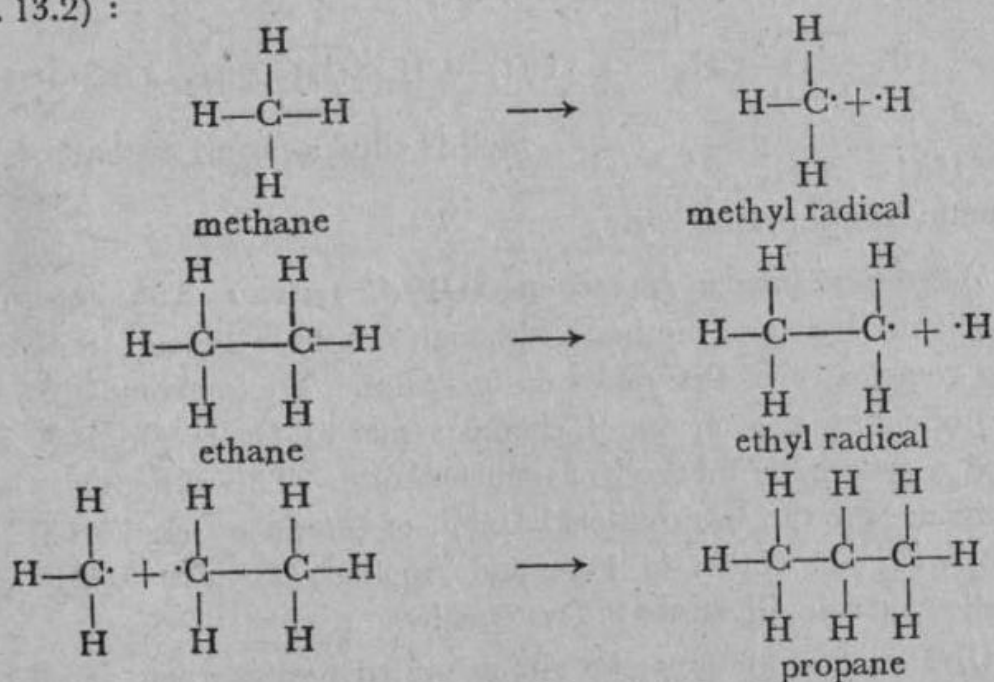


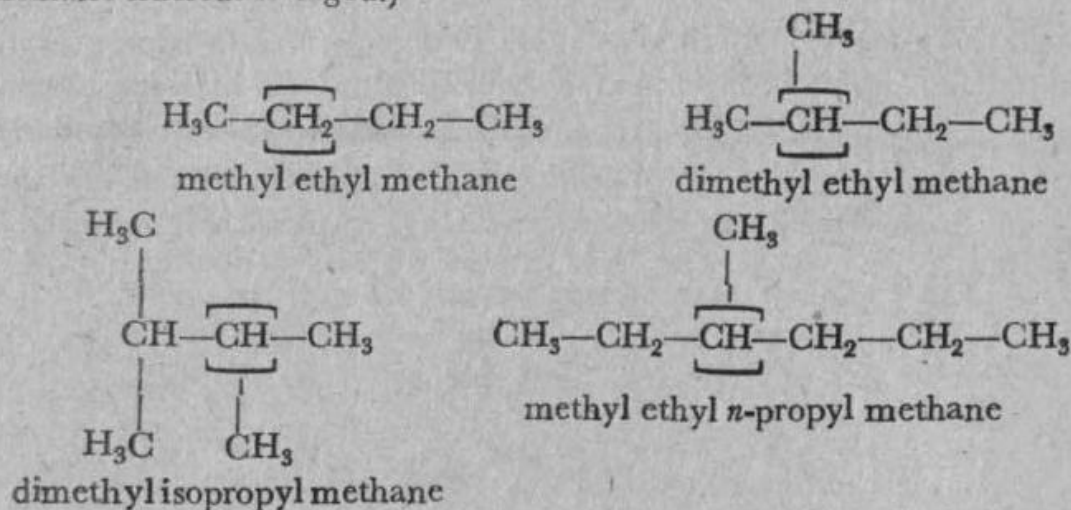
Fig. 13.2

Radicals which are derived from alkanes by removal of a hydrogen atom are known as *alkyl-radicals*. The radical names are derived from the parent hydrocarbon by substituting *-ane* ending with *-yl*. An alkyl radical is symbolized as R when the general formula of a family of compounds is written.

(a) Nomenclature based on Methane: Two systems of nomenclature are generally followed. The one assumes the carbon compounds to be derived from methane. The following rules help in naming a hydrocarbon as a derivative of methane :

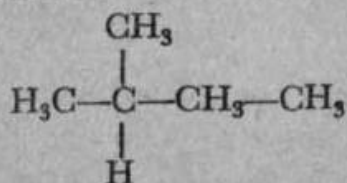
- (i) The carbon atom attached to the largest number of other carbon atoms is selected as the 'methane carbon', and each radical attached to this carbon is used as a prefix to methane.
- (ii) The radicals are arranged according to size with the smallest coming first.
- (iii) Two of the same radicals are indicated by prefix *di-*, three by *tri-*, and four by *tetra*.

This system is illustrated by the following examples. (The methane nucleus is caged.)



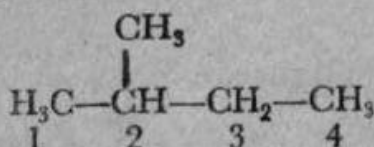
(b) **Nomenclature based on IUPAC rules :** The system of nomenclature based on methane, although simple is difficult to observe as the complexity of the molecule increases. To overcome this and other difficulties a congress of chemists met at Geneva in 1892 and evolved a systematic method of nomenclature. This system was later on amended by the International Union of Chemistry (I. U. C.) and the International Union of Pure and Applied Chemistry (IUPAC). The following rules illustrate the systems :

- (i) The general name for the saturated hydrocarbons is alkane. Names of the first ten alkanes have been given in table 13.1.
- (ii) For a branched chain hydrocarbon, determine the longest continuous chain of carbon atoms in the molecule. Use the name of the saturated hydrocarbon corresponding to this number of carbon atoms. Thus in the compound



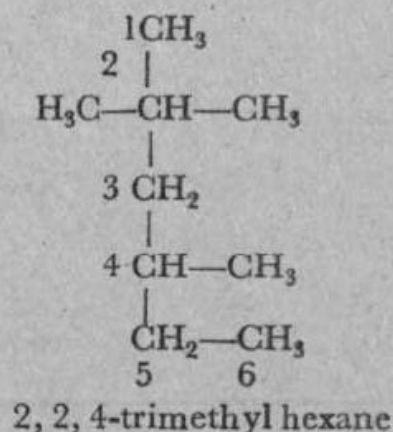
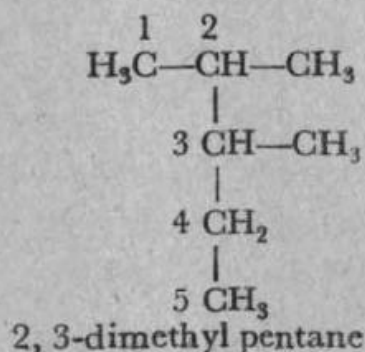
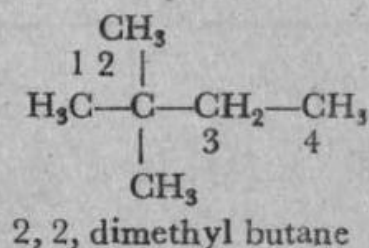
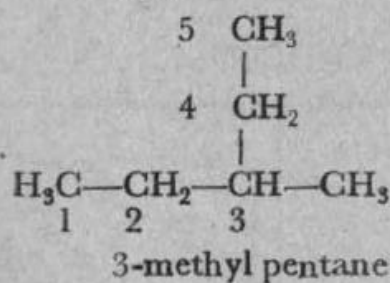
the longest chain consists of four carbon atoms, hence the basis for its nomenclature would be butane.

- (iii) Number the carbon atoms of the continuous chain beginning at the end nearest the branching. The above compound would then be numbered as :



- (iv) The substituents other than hydrogen atoms are given names (radical names) and numbers. The name of a substituent is taken from the saturated hydrocarbon with the same number of carbon atoms by changing the *-ane* ending to *-yl*. The above compound would then become : 2-methyl butane (number 2 signifies the point of attachment of the methyl group).

Following examples illustrate the system :



Thus the common names of alkenes and alkynes are derived by substituting the ending *-ane* (of the corresponding alkane) with *-ene* and *-yne* respectively. Moreover, the selection of the longest chain is such that it contains the multiple bond, and the number used to locate the multiple bond is the *lower* of the two numbers assigned to the doubly bonded carbon atoms.

SATURATED HYDROCARBONS

Occurrence : Natural gas and petroleum are important sources of alkanes. The world production of petroleum is estimated at more than 5.6 billion barrels of 42 gallons each, and is widely distributed. However, the Middle East, the United States of America, Venezuela and the U. S. S. R. produce about 87% of the total world output.

Petroleum is a mixture of a large number of hydrocarbons of different families. Their separation is usually very difficult. For

example, it has been estimated that the portion of petroleum boiling up to 200°C contains at least 500 compounds. Petroleum constitutes the principal source of alkanes up to C_{40} as well as other types of compounds.

Instead of isolating individual compounds, petroleum is *fractionally distilled*, these fractions are indicated in the following table 13.3 :

Table 13.3
FRACTIONATION OF PETROLEUM

Fraction	B. P. ($^{\circ}\text{C}$)	Alkane Content
Gas	below 20	$\text{C}_1\text{—C}_4$
Petroleum ether	20—60	$\text{C}_5\text{—C}_6$
Light naphtha	60—100	$\text{C}_6\text{—C}_7$
Gasoline (petrol)	40—200	$\text{C}_5\text{—C}_{10}$
Kerosene	175—325	$\text{C}_{11}\text{—C}_{18}$
Gas oil	300—500	$\text{C}_{15}\text{—C}_{40}$
Lubricating oil	above 400	

Pakistan has limited deposits of petroleum in the Chakwal district of Rawalpindi region.

Natural gas consists largely of methane (between 70–85%), but it also contains, among other gases, small amounts of ethane, propane and butanes. Propane and butanes are separated by cooling when these are liquefied.

Pakistan has huge reserves of natural gas at Sui, in Baluchistan and at other places. The same are now commercially exploited.

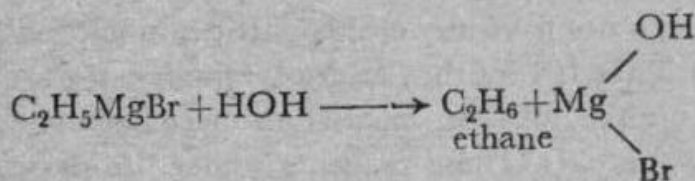
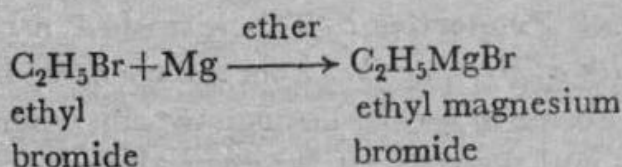
Methane is also formed during the decomposition of vegetable matter under water in marshes, hence the common name *marsh gas*.

Synthesis of Alkanes. (1) In a laboratory alkanes may be obtained from alkyl halides (see Chapter 14 for the preparation of alkyl halides).

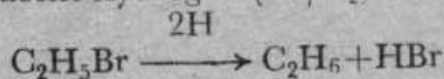
Three routes are available.

(a) **Hydrolysis of Grignard's Compounds :** An Italian chemist

Grignard (1911) prepared alkyl magnesium halides by the direct action of alkyl halides on magnesium turnings. These compounds are hydrolysed by water forming alkanes :

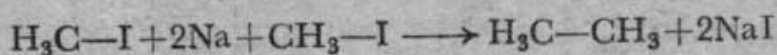


(b) **Reduction of Alkyl Halides :** An alkyl halide on reduction gives an alkane with nascent hydrogen (Zn/H_2)



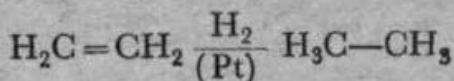
A mixture of Zn and HCl constitutes a good reducing agent.

(c) **Wurtz Reaction :** A French chemist, Wurtz (1855), prepared ethane by treating methyl iodide with sodium metal :



Wurtz reaction is fairly general, and is used in the preparation of symmetrical alkanes having twice as many carbons as the original alkyl halide.

(2) **Catalytic Reduction of Alkenes :** The double bond of an alkene will add hydrogen *quantitatively* in the presence of platinum, palladium or nickel as catalyst forming an alkane with the same carbon skeleton.



With platinum or palladium the reaction takes place at ordinary temperature, but nickel requires a pressure of 1000—2000 psi and temperature from 100 to 200°C.

PROPERTIES

(a) **Physical Properties :** At ordinary temperature and pressure the first four members are gases, whereas those with more than twenty carbon atoms are wax-like solids. The intermediate compounds are colourless liquids, lighter than water.

Isomeric hydrocarbons have different physical properties. Usually, more branched hydrocarbons have lower boiling points. Alkanes are insoluble in water, but soluble in organic solvents.

(b) **Chemical Properties :** The historical name, *paraffins* (in Latin it means *little affinity*), derives from the chemical inertness of these compounds. The alkane molecules do not have any atoms with unshared pairs of electrons and the covalent bonds in alkanes are not polarized. Therefore alkanes do not have any electrophilic or nucleophilic centres in their molecules. This is why they are not reactive towards reagents such as aqueous acids, alkalies, potassium permanganate, bromine water, and halogen acids. These reagents under ordinary conditions react as electrophiles or nucleophiles. However alkanes react with oxygen when ignited and also react with halogens, and with concentrated nitric acid.

(i) **Combustion :** When ignited in air, alkanes burn giving rise to CO_2 and H_2O .



The process of burning evolves considerable heat (called the heat of combustion) which forms the basis of the fuel value of hydrocarbons.

(ii) **Halogenation :** Alkanes are saturated compounds, hence the only manner in which reactions can occur is by displacement or substitution of one atom or group by another. Chlorine or bromine react very slowly with alkanes at room temperature. At higher temperatures, and in the presence of sunlight, the hydrogen atoms in the hydrocarbon can be replaced by halogen atoms. Such reactions (*photo-chemical* in character) are called *halogenation reactions*. The probable course of the reaction may be represented as (Fig. 13.3).

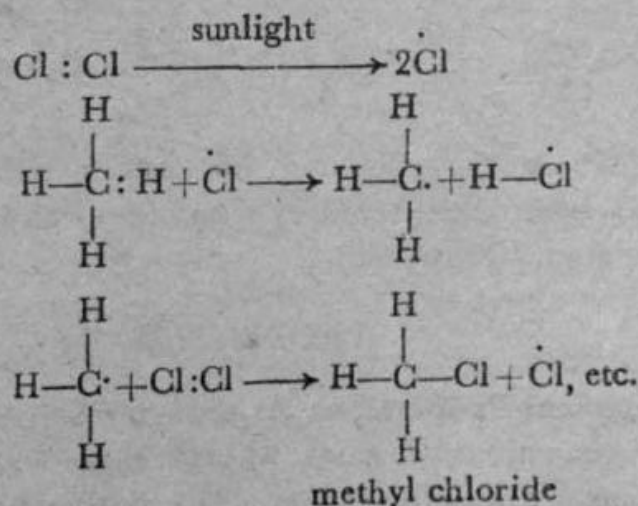
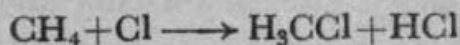
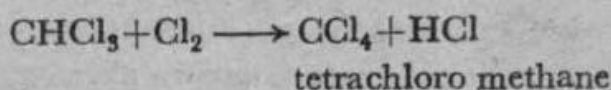
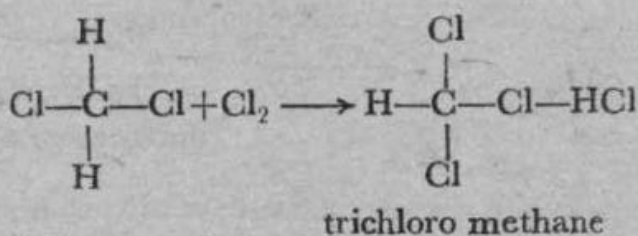
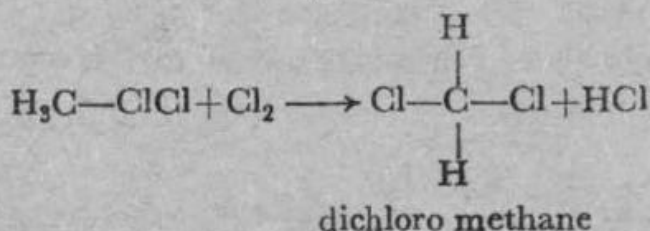


Fig. 13.3

The overall equation may be summed up as.

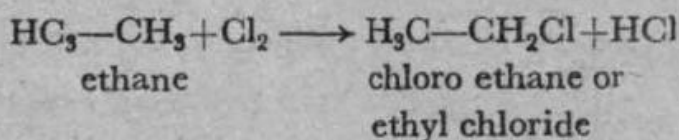


The above reaction, very frequently, gives rise to *side reactions*. For example, the methyl chloride formed as above may react further with chlorine giving rise to the following products :

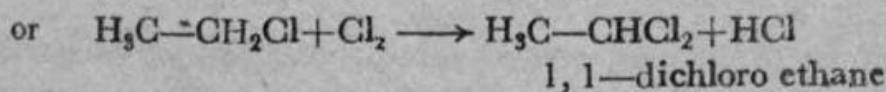
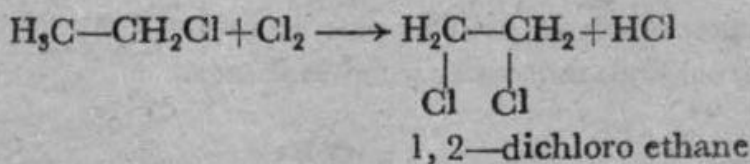


In practice a mixture of products is obtained. Dichloromethane, trichloromethane and tetrachloromethane are commonly called methylenechloride, chloroform and carbon tetrachloride respectively.

With ethane, the process of halogenation may become even more complex :



However, replacement of the second hydrogen may give two products :

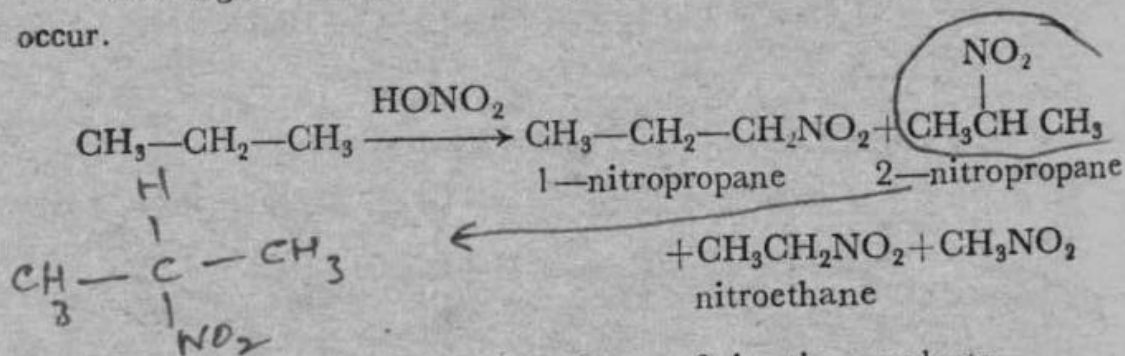


Because of the multiplicity of products, halogenation of alkanes is not a useful laboratory reaction.

(iii) **Nitration** : When a mixture of an alkane and nitric acid vapour is passed, rapidly, through a narrow metal tube at 400—450°C, one hydrogen atom on the alkane is substituted by one nitro group ($-\text{NO}_2$).

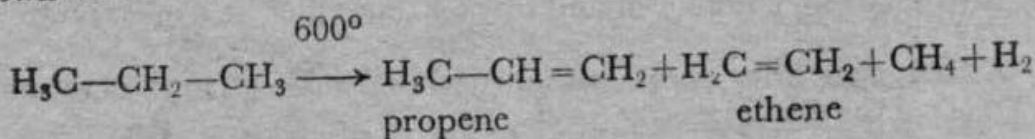


With higher alkanes breaking up of carbon—carbon bond may occur.

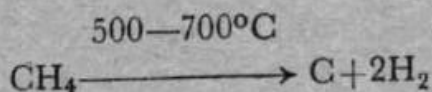


Larger alkanes yield complex mixture of nitration products.

(iv) **Pyrolysis or Cracking :** Alkanes are generally stable, but if heated well above their boiling points in absence of air, the molecules may be split up or 'cracked' into smaller molecules. Thus when propane is passed through a hot metal tube at 500—700°C it breaks down as :



Methane gives carbon black : When heated strongly in the absence of air :



Carbon black is used as a filler in tyre manufacture.

Cracking process is used in petroleum industry for making more motor fuel from high molecular weight alkanes.

ALKENES

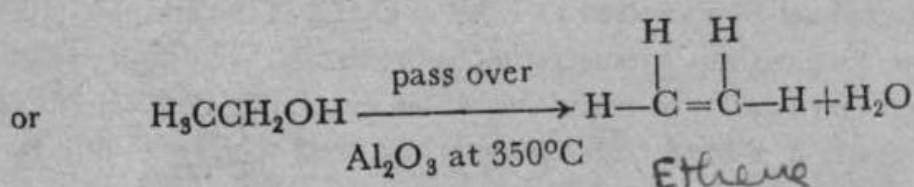
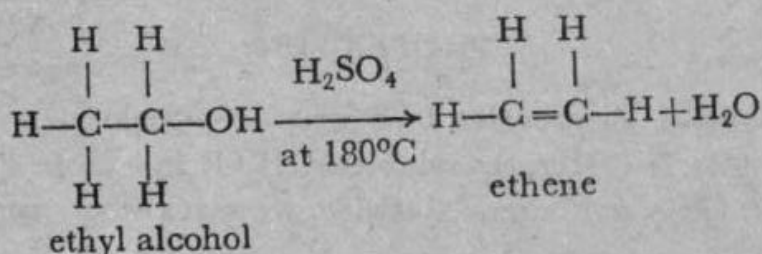
In contrast to alkanes, many hydrocarbons add various reagents and are therefore called 'unsaturated'. There are two important types ; alkenes or olefins, and alkynes or acetylenes. The commercial source of alkenes up to C_4 is by cracking of petroleum (see above).

However, these and the higher alkenes are obtained by synthetic methods also.

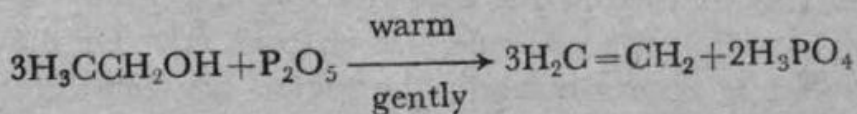
SYNTHESIS OF ALKENES

Alkenes are prepared by three principal methods.

(i) **By Dehydration of Alcohols :** On heating with an acid catalyst (such as H_2SO_4 or H_3PO_4) or heating at high temperature, with Al_2O_3 , alcohols undergo loss of water forming alkenes :

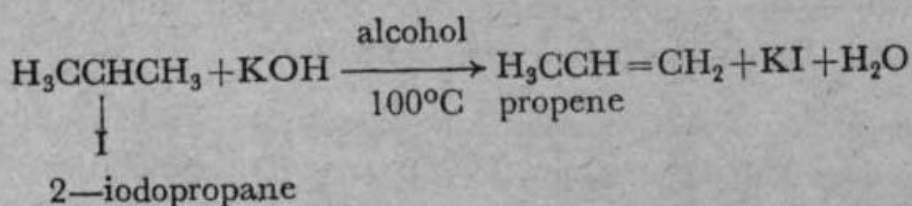


Even P_2O_5 may be employed :



Alkene formation is more rapid with tertiary than with primary alcohols. Dehydration of alcohols is not a good synthetic route as isomeric alkenes are produced from higher alcohols.

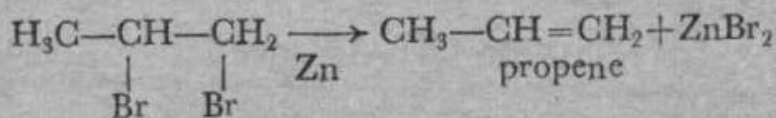
(ii) **By Dehydrohalogenation :** A concentrated solution of KOH in ethyl alcohol removes halogen halide from an alkyl halide ;



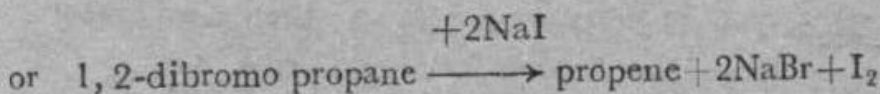
KOH is preferred over NaOH because the former is more soluble in alcohol.

(iii) **Dehalogenation of Vicinal Dihalides :** A compound having two halogen atoms on adjacent carbon atoms is called a vicinal dihalide

(or *vic*-dihalide). Such compounds on treatment with zinc dust or with sodium iodide yield alkenes :



1, 2-dibromo propane



PROPERTIES

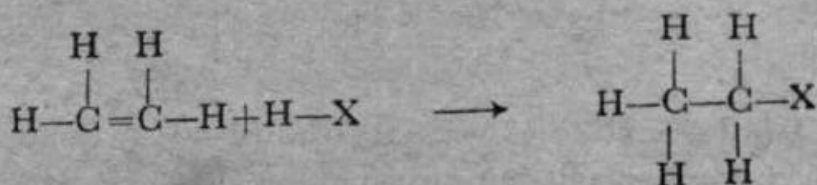
(a) **Physical Properties :** Ethene is a colourless gas with a sweetish taste. It is slightly soluble in H_2O , but more so in organic solvents. Propene and butene, likewise, are gases others are liquids.

(b) **Chemical Properties :** Ethene C_2H_4 , is the simplest alkene. Each of the two carbon atoms is sp^2 hybridized. The four, carbons to hydrogen, σ bonds are made by sp^2-s overlap. Between the two carbons there is a σ bond (sp^2-sp^2 overlap) and a π bond due to $p-p$ parallel overlap.

A π orbital is diffused and is located above and below the plane of the atomic nuclei of the molecule (see chapter II). On the other hand a σ orbital is concentrated in the region between the atomic nuclei. The electrons in a π orbital are, therefore, more exposed to attack by electrophilic reagents than the σ electrons in saturated compounds. Further, a π bond is not as strong as a σ bond. The energy necessary to break a π bond would thus be less than that required to break a σ bond.

Hence the chemical reactivity of alkenes arises from the ease of availability of the π electrons for bond formation with electrophilic atoms. The alkenes thus behave as nucleophiles.

Alkenes, therefore, are very reactive substances and readily add on H_2 , halogens, halogen acids, H_2SO_4 etc. The general pattern of these reactions is shown below :



The reaction of $\text{H}-\text{Br}$ with ethene is described as a typical, case, Fig. 13.4.

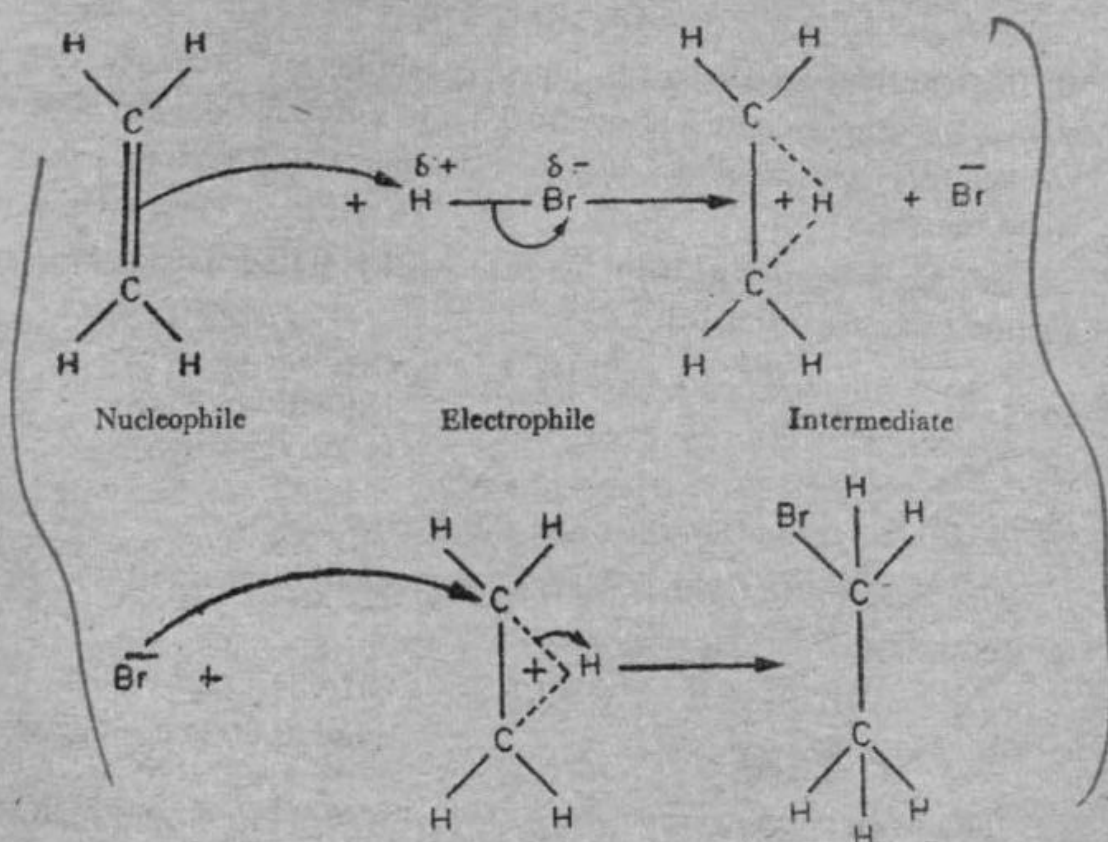


Fig. 13.4

The π electrons are donated to the electrophilic end of the $\text{H}-\text{Br}$ molecule forming a new carbon-hydrogen bond. The nucleophilic bromide ion released in the first step then reacts with the positively charged intermediate to form the product, ethyl bromide.

ADDITION REACTIONS OF ALKENES

(i) **Hydrogen** : As has been observed earlier (P. 193) alkenes add hydrogen in the presence of catalysts forming alkanes.

(ii) **Halogens** : Bromine adds to a double bond to form a 1, 2-dibromide. (Fig. 13.5)

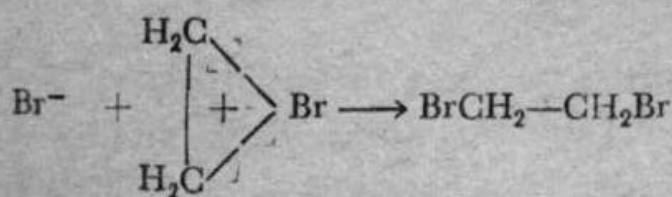
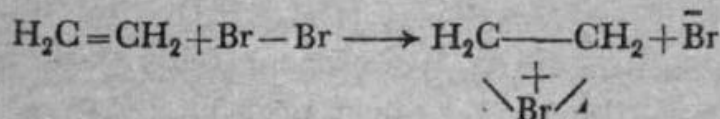
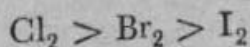


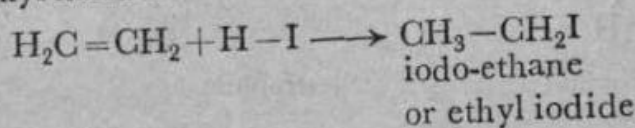
Fig. 13.5

Other halogens behave similarly. However, the ease of addition is in the following order.



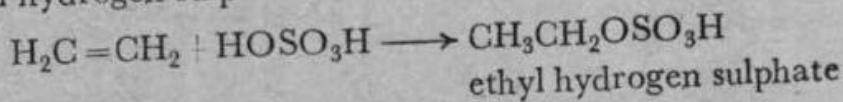
If ethylene is passed into an aqueous solution of bromine, the red colour of bromine is discharged. This is a test for the presence of a carbon to carbon double bond in a compound. The test is done at room temperature.

(ii) **Hydrogen Halide** : As seen earlier, halogen acids react with alkenes to form alkyl halides :

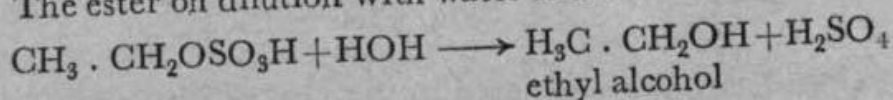


The ease of addition is in the order $\text{HI} > \text{HBr} > \text{HCl}$

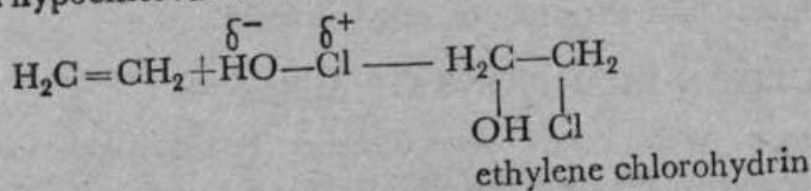
(iv) **Sulphuric Acid** : Alkenes are soluble in concentrated H_2SO_4 forming alkyl hydrogen sulphates :



These sulphate esters are used in preparing alcohols from alkenes. The ester on dilution with water forms alcohol.

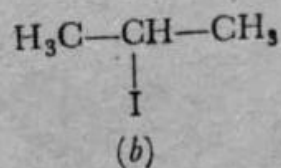
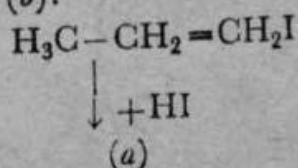


(v) **Hypohalous Acids** : If ethene is bubbled through a solution of hypochlorous acid a chlorohydrin is formed.



MARKOWNIKOFF'S RULE

Addition of HI to a *symmetrical* molecule, like ethene, can result in the formation of only one compound ($\text{CH}_3\text{CH}_2\text{I}$). But if HI is added to an *unsymmetrical* molecule, like propene ($\text{CH}_3-\text{CH}=\text{CH}_2$), the reaction might yield isomeric 1-iodo propane (a) or 2-iodo propane (b).

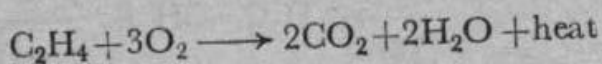


The course of addition, in such cases, is determined by the rule given by a Russian chemist, Markownikoff (1870). Which states that the negative part of the acid, HX, attaches itself to the carbon atom that has the least hydrogen atoms. Therefore addition of HI to propene would form 2-iodo propane in preference to 1-iodo propane.

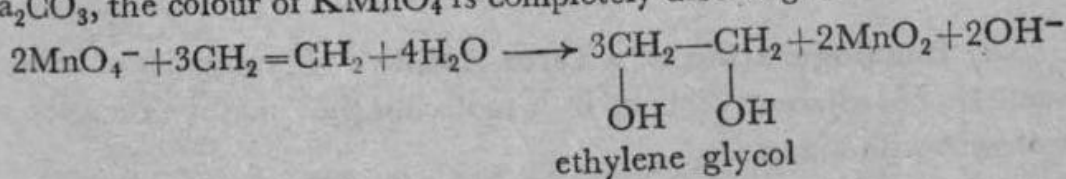
Markownikoff's rule is applicable to addition of an unsymmetrical reagent to an unsymmetrical alkene.

OXIDATION REACTIONS

(i) **Combustion** : Like alkanes, alkenes, are burnt in air to CO_2 and H_2O .



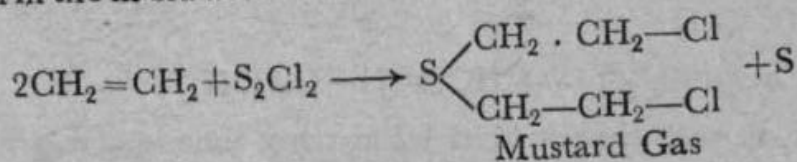
(ii) **Hydroxylation** : When an alkene is passed into a dilute solution of KMnO_4 (purple solution), rendered basic by addition of Na_2CO_3 , the colour of KMnO_4 is completely discharged.



The above reaction constitutes a simple test for the presence of unsaturation in an organic molecule (Baeyer's Test).

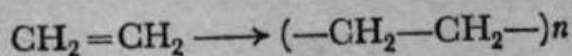
USES :

Ethene is used in deepening the colour of citrus fruit. It is also used in the manufacture of a blistering agent called "mustard gas"



Mustard gas is extremely dangerous to skin and has been employed in warfare.

Under the influence of various catalysts alkenes undergo a self-addition reaction commonly known as "polymerisation". This results in the formation of compounds having many times the molecular weight of the original compound. For example, when ethene is heated above 100°C and under pressure above 15,000 psi, in the presence of 0.01% oxygen, it is converted into a high molecular weight hydrocarbon called *polyethylene*.



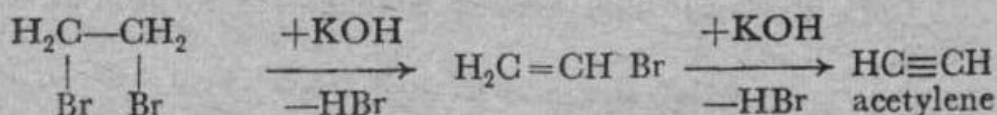
Polyethylene is used chiefly in the manufacture of thin sheets, wire insulation and plastic pipes.

ALKYNES OR ACETYLENES

Of the three types of hydrocarbons, alkynes rarely occur in nature. In fact only the first member, ethyne or acetylene (C_2H_2), is important commercially.

SYNTHESIS OF ALKYNES

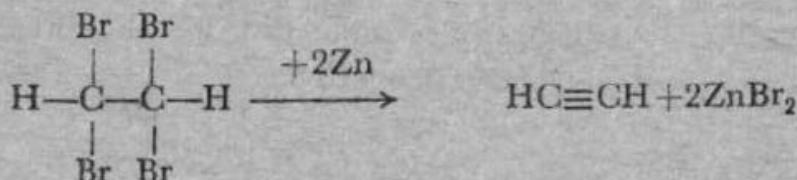
(i) **Dehydrohalogenation of a Dihalide**: Removal of two halogens on adjacent carbon atoms gives an alkyne.



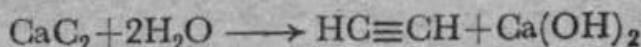
1, 2—dibromoethane

Alcoholic KOH is used to bring about the reaction.

(ii) **Dehalogenation of a Tetra Halide**: If two pairs of halogen atoms lie on adjacent carbons in a molecule they may be removed on treatment with zinc dust.



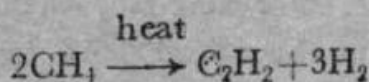
Ethyne or Acetylene is usually prepared by the action of water on calcium carbide (CaC_2).



Calcium carbide, in turn, is prepared by heating lime and carbon in an electric furnace.



This preparation of acetylene is a good example of the synthesis of an organic compound from elements. Acetylene is also obtained when methane is heated to $1400-1600^\circ C$.



(a) Physical Properties :

Physical properties resemble those of alkenes. However, the boiling points are somewhat higher and the solubility in water is greater than alkenes.

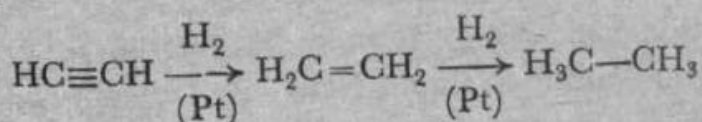
(b) Chemical Properties :

It was shown in Chapter 12 that the carbon atoms in acetylene are sp hybridized. The carbon to hydrogen σ bonds are due to $sp-s$ overlap and the two carbon atoms are joined by an $sp-sp$ σ bond and two π bonds. Hence the reactions of alkynes are of the same type as those of alkenes.

ADDITION REACTIONS

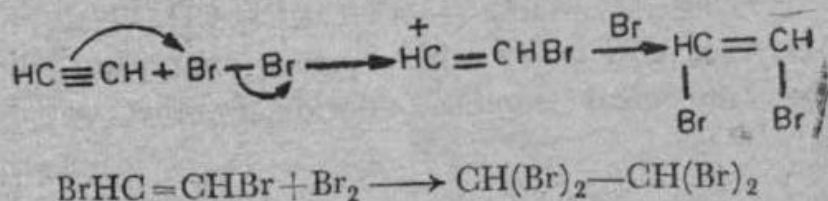
Alkynes undergo addition reactions similar to those of alkenes. However, these add two molecules of reagent instead of one common to alkenes.

(i) **Addition of Hydrogen :** Hydrogenation of an alkyne in the presence of Pt or Ni gives an alkane through the intermediate formation of an alkene.



The addition can be stopped at the alkene stage

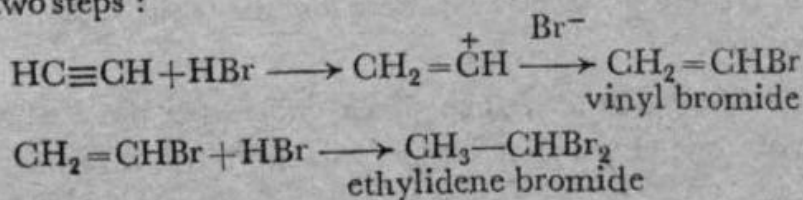
(ii) **Addition of Halogens :** Halogens similarly add to alkynes giving tetra halogen compounds :



Reaction can be stopped at the dihalide stage.

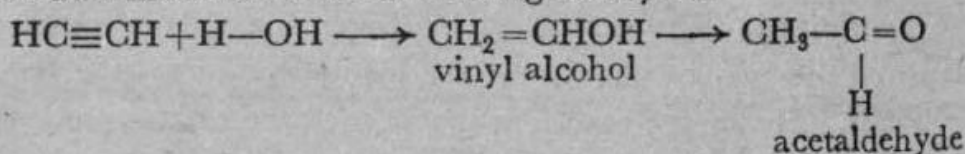
Cl_2 reacts violently, whereas reaction with I_2 is slow. (In fact iodine reacts with ethyne at 150° in a sealed tube giving 1,2-diiodoethene).

(iii) **Addition of Halogen Acids :** Here again addition takes place in two steps :



(Note that addition of the second molecule of HBr takes place in accordance with the Markownikoff's rule).

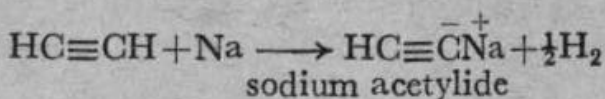
(iv) **Addition of Water :** In the presence of HgSO_4 and H_2SO_4 alkynes add a molecule of water forming aldehydes.



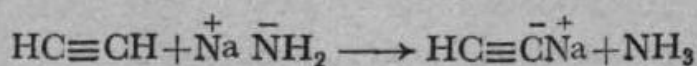
The intermediate 'vinyl alcohol' then probably rearranges to form acetaldehyde.

(b) Reactions of Hydrogen Atoms

(i) If one of the alkyne carbon atoms bears a hydrogen atom, this hydrogen is replaceable by metals, chiefly sodium. The procedure is to pass alkyne over molten sodium (110°C).



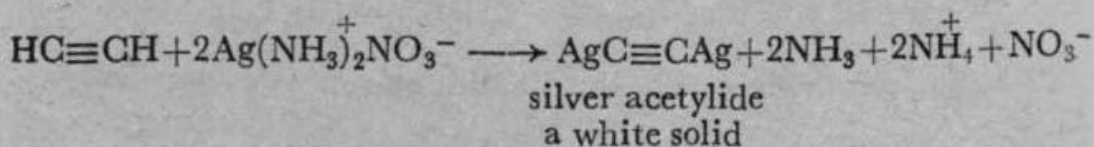
Sodium acetylide can also be formed by passing C_2H_2 into a dilute solution of sodium amide in liquid NH_3 .



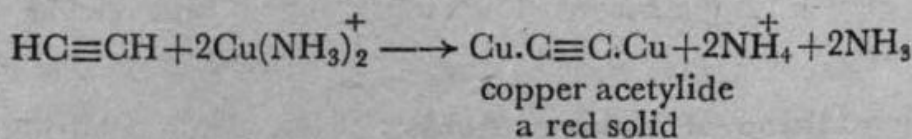
Sodium acetylides are useful reagents in the preparation of higher alkynes :



(ii) Acetylene also reacts with aqueous ammonical silver nitrate or aqueous ammonical cuprous chloride forming water insoluble acetylides :



and



In these reactions acetylene acts as an acid. The acetylides explode when dry.

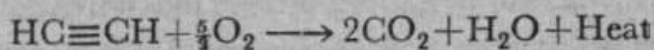
Acetylide formation can take place only with those alkynes that have at least one hydrogen atom attached to a triply bonded carbon.

Acetylides generate acetylene on treatment with HNO_3 :



COMBUSTION

Combustion of ethyne is a commercially important reaction because this is accompanied by a bright white light and a large amount of heat.



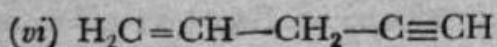
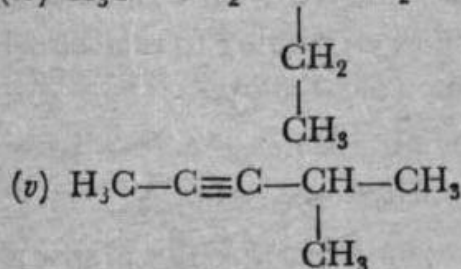
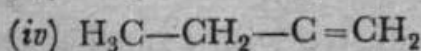
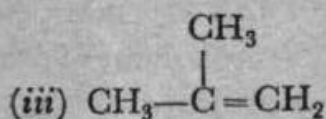
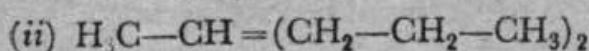
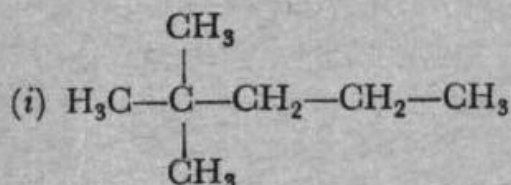
USES OF ACETYLENE

1. Oxy acetylene flame is used for welding purposes. It has a temperature in the region of 2800°C .

2. Acetylene is an important source of organic chemicals. Acetylene dichloride and tetrachloride are important solvents. Acetaldehyde is a starting material for a large number of chemicals. Addition of acetic acid gives vinyl acetate, which is used as a plastic. Addition of hydrogen cyanide gives acrylonitrile which is used for the production of synthetic fibres.

Questions

1. Name each of the following by the IUPAC system :



2. Write structural formulas for :

- (i) 2-bromo-3-methyl pentane.
- (ii) 1-chloro-3, 3-dimethyl butane.
- (iii) 3, 4-dimethyl 2-hexene.
- (iv) 2, 2, 3, 5, 6-penta methyl-3-heptene.
- (v) dimethyl acetylene.
- (vi) 3-ethyl-1-hexyne.

3. Write structural formulas for the five isomeric hexanes (C_6H_{14}), six isomeric pentenes (C_5H_{10}), and three isomeric pentynes (C_5H_8).
4. Write electronic structures for the following :
 - (i) chloroform,
 - (ii) nitromethane,
 - (iii) ethylene chlorohydrin,
 - (iv) vinyl bromide,
 - (v) sodium acetylide,
 - (vi) methyl magnesium iodide.
5. Which alkane may be obtained by the reduction of :
 - (i) 2-bromobutane,
 - (ii) 1-bromobutane, and
 - (iii) 2-bromo, 3-methylpentane.
6. What hydrocarbon would be formed by the action of sodium metal on :
 - (i) ethyl iodide,
 - (ii) 2-iodo propane, and
 - (iii) 2-bromo butane?

Name the products according to the IUPAC system.

7. A certain volume of methane at 20°C and 740 mm pressure weighs 5g. Calculate the weight of the same volume of propane measured at the same temperature and pressure.
8. A sample of *n* butane is contaminated with a small amount of 1-butene. What method would you employ to remove 1-butene and thus obtain a pure specimen of *n*-butane?
9. Write structural formulas for all alkenes that can be reduced to 2-methyl butane by catalytic hydrogenation.
10. Which alkyl chloride would you select for the preparation of 1-butene by reaction with alcoholic KOH : 1-chlorobutane or 2-Cl-butane.
11. An alkyl chloride, $C_5H_{11}Cl$, was recovered unchanged after heating with alcoholic KOH. What is its most likely structure?
12. Addition of bromine to 5 litres of ethene at room temperature and normal pressure gives 30g. of 1, 2-dibromoethane. Calculate the percent age yield of the product.

13. A sample of 2.1 g of a hydrocarbon reacts with 60 ml of a solution of bromine in carbon tetrachloride, which contains 5.0 g of bromine per 100 ml. What is the equivalent weight of the hydrocarbon? If the molecular weight of the hydrocarbon be 56, what must be its structure? Is there a possibility of skeletal isomerism?
 14. Suggest chemical means of distinguishing between :
 - (i) propane and propene,
 - (ii) 1-butene and 1-butyne, and
 - (iii) 1-butyne and 2-butyne.
 15. A hydrocarbon, C_4H_6 , absorbs two moles of hydrogen in the presence of platinum as a catalyst. The reduction product is inert towards bromine and potassium permanganate. Draw possible structures for C_4H_6 . What further information is necessary in order to establish the identity of the hydrocarbon?
 16. How would you prepare :
 - (i) Propyne from propene,
 - (ii) Propyne from acetylene, and
 - (iii) Ethane from ethene?
 17. A hydrocarbon, C_5H_8 obtained by the action of alcoholic KOH on 3, 3-dichloro-2,2 dimethyl butane, adds two molecules of Br_2 and does not give a precipitate with ammonical silver nitrate solution. What is its structure most likely?
 18. For what alkyne does the volume of gases formed in its combustion equal the volume of gases burnt?
 19. What is the shortest alkyne molecule in which all the atoms are linear?
 20. Write equations for reaction between :
 - (i) 1-pentene and hydrogen chloride
 - (ii) propene + concentrated H_2SO_4
 - (iii) *n*-butane + HNO_3
 - (iv) ethyne + alkaline potassium permanganate
 - (v) ethyne + hydrocyanic acid
 - (vi) propyne + iodine
 - (vii) ethane + HNO_3 .
-

CHAPTER 14

MONOHALO—ALKANES (ALKYL HALIDES)

The family of compounds which have the general molecular formula $C_nH_{2n+1}X$, where $X = F, Cl, Br$ and I , is called *monohalo-alkanes* or *alkyl halide*. They may be regarded as having been derived from alkanes (C_nH_{2n+2}) by replacing a hydrogen atom with a halogen atom. As mentioned in Chapter 11, they are classified into primary, secondary, and tertiary alkyl halides.

One method for naming the alkyl halides consists in first writing the name of the alkyl group to which the halogen atom is attached and then writing the name of the halide ion corresponding to the halogen atom present. For example, in the compound CH_3-Cl , the name of the alkyl group (CH_3) to which the halogen is attached is *methyl* and the halide ion corresponding to chlorine is the *chloride* ion. Therefore the name of the compound CH_3-Cl is *methyl chloride*. For a secondary alkyl halide the prefix *sec*- and for a tertiary halide the prefix *ter*- is added before the name.

Another method of naming is the IUPAC system in which alkyl halides are named as derivatives of alkanes. CH_3-Cl is called *chloromethane*. The names and structural formulas of a few simple alkyl halides are given below :

CH_3-Cl
methyl chloride

or

chloromethane
b.p., $-24^\circ C$

CH_3CHCH_3
|
Cl
isopropyl chloride

or

sec-propyl chloride

or

2-chloropropane b.p., $36.5^\circ C$

CH_3CH_2Cl
ethyl chloride

or

chloroethane
b.p., $12.5^\circ C$

$CH_3CH_2CH_2Cl$
n-propyl chloride

or

1-chloropropane
b.p., $47^\circ C$

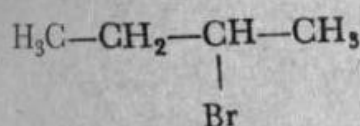
$CH_3CH_2CH_2CHBr$

n-butyl bromide

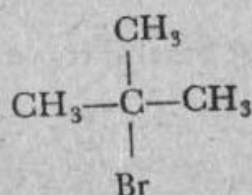
or

1-bromobutane

b.p., $101.6^\circ C$



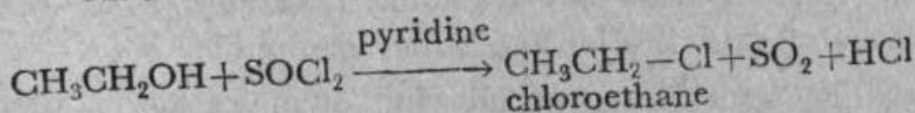
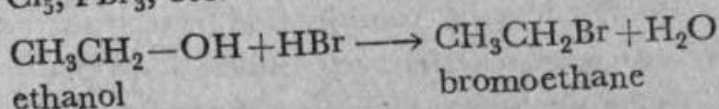
sec-butyl bromide
or
2-bromobutane
b.p., 68°C



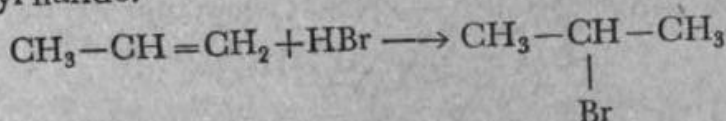
ter-butyl bromide
or
2-bromo-2-methyl propane
b.p., 73.3°C

PREPARATION

(1) **From Alcohols :** The most commonly used method for the preparation of alkyl halides is by the reaction of alcohols with halogen acids or with inorganic acid halides such as SOCl_2 (thionyl chloride), PCl_5 , PBr_3 , etc.



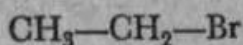
(2) **From Alkenes :** Addition of a halogen acid to an alkene gives an alkyl halide.



2-bromopropane

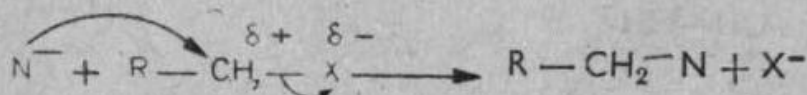
REACTIONS

(1) **Nucleophilic Substitution Reactions :** The chemical reactivity of alkyl halides stems from the fact that the C-X bond is polarized due to the greater electronegativity of a halogen atom as compared to a carbon atom. For example, in



the carbon atom attached to halogen carries a small positive charge. As pointed out in Chapter 11, such a carbon atom is said to be *electrophilic* in nature. It will have a tendency to accept a pair of electrons from a nucleophilic reagent and form a new bond. In doing so this carbon atom will break its old bond with the halogen atom. Thus, the new nucleophile will take the place of the halogen atom.

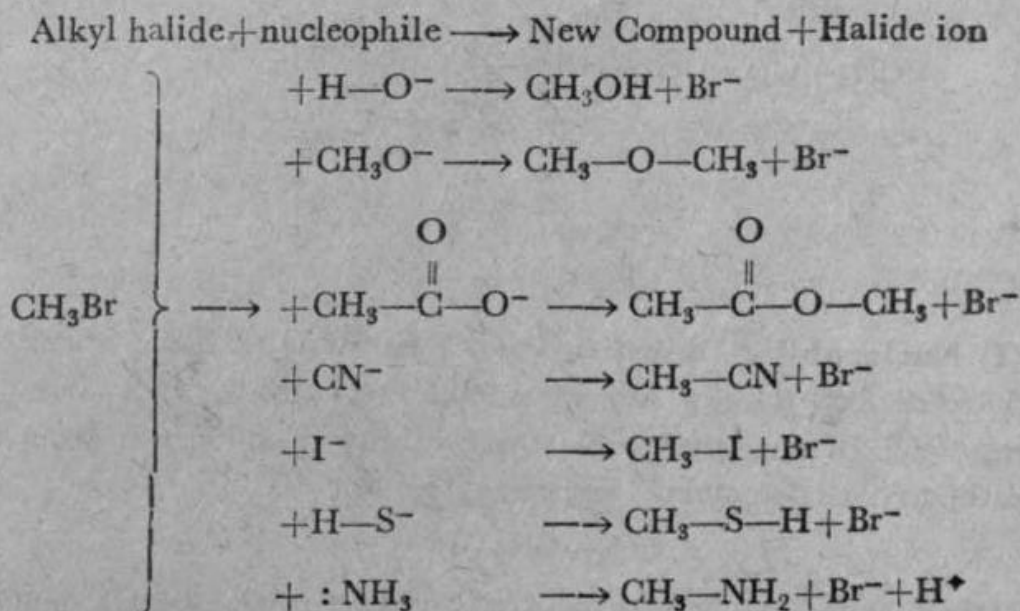
A general representation of the reactions of this type is



The reagent, N^- , is called an attacking *nucleophile*, $\text{RCH}_2\text{-X}$ which contains the electrophilic atom is called as *substrate* and X^- (the halide ion), which is also a nucleophile, is called the *leaving group*. The curved arrow from the minus sign of N to the carbon atom indicates that N^- donates a pair of electrons to form a new bond between N and carbon. The curved arrow on the C-X bond indicates that the two electrons making the C-X bond will be donated to the halogen atom to form a halide ion.

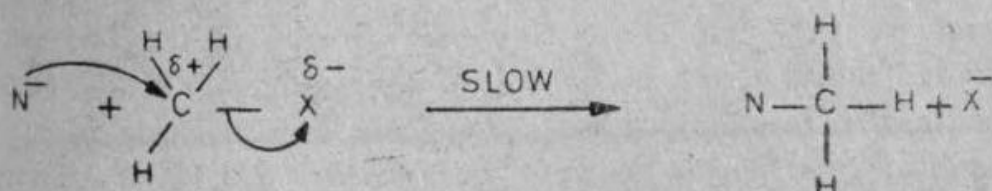
The net result of the reaction is that one nucleophile (N^-) displaces another nucleophile (X^-) from combination with an electro-philic atom. Such displacement reactions are called *Nucleophilic Substitution* reactions. In short hand they are simply referred to as *SN* reactions, where *S* stands for substitution and *N* for nucleophilic.

It will be seen from the following examples how a variety of nucleophiles react with an alkyl halide to form different types of organic compounds.



The SN reactions of alkyl halides may occur in a *single* step or in *two* steps. In the one step SN reactions the new bond between the attacking nucleophile and the electrophilic carbon atom is formed at the same time at which the old bond between this carbon atom and the halogen atom is broken. In other words the attack of N^- on

carbon and the departure of the halide ion takes place simultaneously in a *single step* :



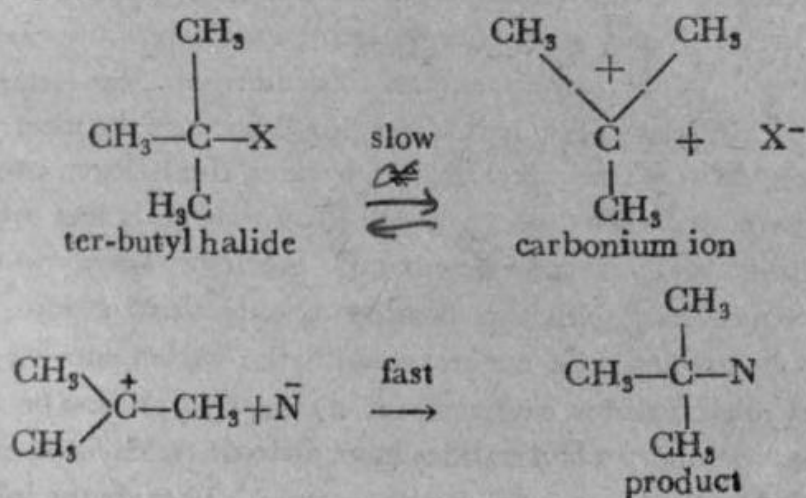
Obviously this step would also be the *rate determining* step of the reaction, *i.e.*, the step in which bond making and bond breaking processes occur simultaneously, determines the overall rate of the reaction. A reaction in which two molecules react together in the rate determining step is called a *bimolecular* reaction. The one step S_N reactions are therefore bimolecular and are called bimolecular nucleophilic substitution reactions or S_N2 reactions where 2 stands for "bimolecular".

The rate of an S_N2 reaction will depend on the concentration of the attacking nucleophile (N^-) as well as on the concentration of the substrate ($R-X$). The rate expression is given by the following

$$\text{Rate} = k [R-X] [N^-]$$

equation where k is the specific reaction rate constant and brackets denote concentrations of the species enclosed within them. Concentrations are usually expressed in moles per liter.

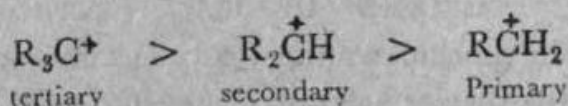
The second type of S_N reactions occur in two discrete steps. In the first step, the $C-X$ bond breaks reversibly to give rise to a positively charged ion and a halide ion. In the second step the positively charged ion reacts with the attacking nucleophile (N^-) to give the product.



The first step is usually very slow as compared to the second step. Therefore in such reactions the rate of formation of the product will depend on the first step. In other words, in the two step S_N reactions, the first step is the rate determining step of the reaction. Since in the rate determining step only one molecule is reacting the overall reaction is said to be *unimolecular*. The two step S_N reactions are called S_N1 reactions where 1 stands for unimolecular. The rate of an S_N1 reaction depends only on the concentration of the substrate (R-X) and *not* on the concentration of the attacking nucleophile.

$$\text{Rate} = k [R-X]$$

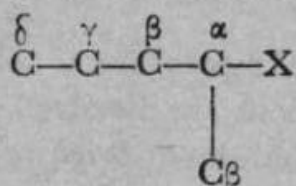
The positively charged ion formed in the first step of an S_N1 reaction has a positive charge on a carbon atom which is bonded to three other groups. Such a cation is called a *carbonium ion*. Tertiary carbonium ions are more stable than secondary carbonium ions which are in turn more stable than primary carbonium ions. The order of stabilities, therefore, is:



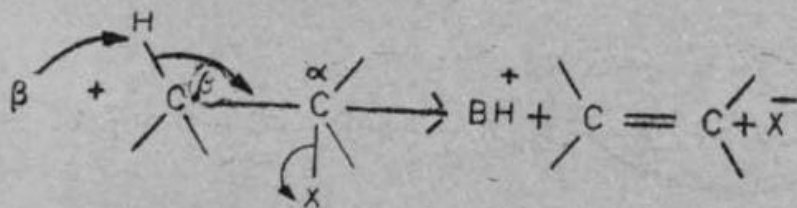
Reactions of primary alkyl halides with nucleophiles are generally S_N2 reactions, whereas those of tertiary alkyl halides are generally S_N1 reactions. Reactions of secondary alkyl halides may be S_N1 or S_N2 , depending on the nature of solvent in which the reaction is carried out and the structure of reactants. Polar solvents aid the ionization step in S_N1 reactions. Formation of carbonium ions is always a difficult process but in highly polar solvents the more stable tertiary carbonium ions are formed to a limited extent. Furthermore, the attack of a nucleophile on a tertiary alkyl halide is difficult because the electrophilic carbon is bonded to three alkyl groups besides the halogen atom and there is no space available through which the nucleophile can approach the electrophilic atom to form a new bond. Steric crowding around the planar carbonium ion, which is bonded to only three groups, is less serious and the nucleophile can react with the carbonium ion easily. Thus tertiary alkyl halides cannot react by the S_N2 process because of steric reasons. Primary alkyl halides have at least two hydrogen atoms directly bonded to the electrophilic carbon atom. Because the hydrogen

atoms are small sized, they do not hinder the approach of a nucleophile to the carbon atom to which they are attached.

2. Elimination Reaction : The carbon atom directly bonded to the halogen atom in an alkyl halide molecule is sometimes called an α (alpha) carbon atom. A carbon atom adjacent to the α carbon atom is called a β (beta) carbon atom and so on e.g.,



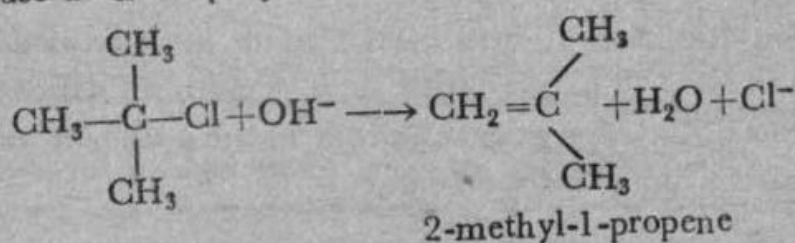
A consequence of the presence of a partial positive charge on the α carbon (due to the polarization of the C-X bond) is that the α carbon atom exerts greater attraction on the electron pair of the bond between C_{α} and C_{β} as compared to the β carbon atom. Thus the $\text{C}_{\alpha}-\text{C}_{\beta}$ bond is also polarized creating a small positive charge on the β carbon atom. If there is a hydrogen atom, bonded to the β carbon, the C-H bond is also polarised such that a slight positive charge may rest on the H atom. The hydrogen atoms linked to the β carbon are, therefore, electrophilic or acidic in nature and can accept a pair of electrons from a base, the result being as follows :



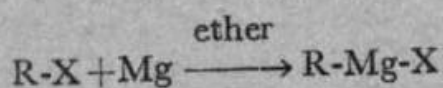
The attacking base removes a proton from the β carbon simultaneously with the formation of a double bond (between C_{α} and C_{β}) and the loss of the halide ion.

The net result is the loss on one H-X molecule (*dehydrohalogenation*) from the alkyl halide molecule. Such reactions in which two groups are eliminated from two adjacent atoms are called β -eliminations. The dehydrohalogenation of an alkyl halide with a base occurs in a single step and is bimolecular. Bimolecular eliminations are symbolized as E2 reactions where E is for elimination and 2 for bimolecular (compare with $\text{S}_{\text{N}}2$).

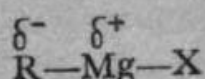
E2 reactions of alkyl halides with bases such as OH^- or $\text{C}_2\text{H}_5\text{O}^-$ are useful in the preparation of alkenes, e.g.



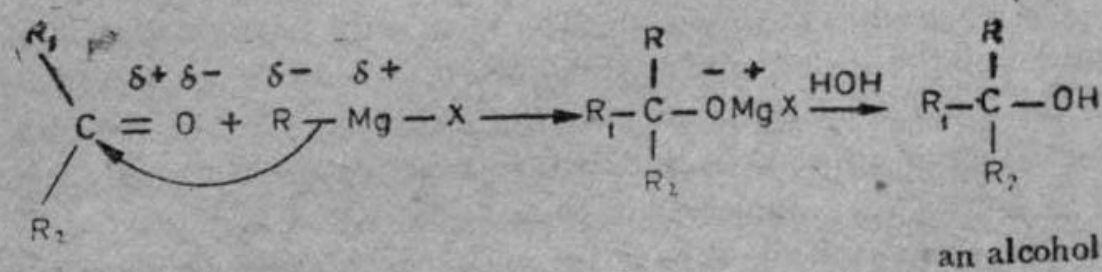
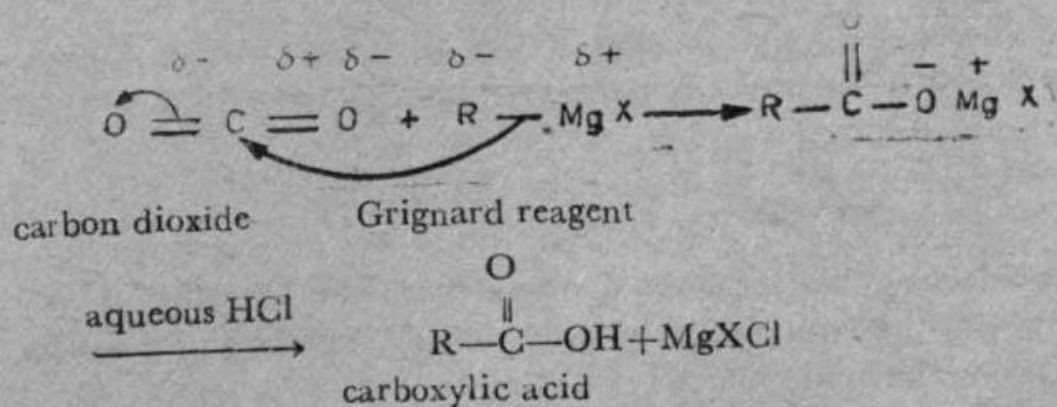
3. Reaction with Magnesium: Alkyl halides react with metallic magnesium when both are dissolved in ether to give what are known as alkyl magnesium halides or *Grignard reagents*:



The structure of alkyl magnesium halides is not completely understood, but most of their reactions are explained on the bases that the carbon-Mg bond is polarized due to the electropositive character of the metal.



The carbon atom bonded to the metal atom bears a partial negative charge and will react with electrophilic compounds to make new bonds. Because of this fact Grignard reagents are of great synthetic value. Two examples are cited below:

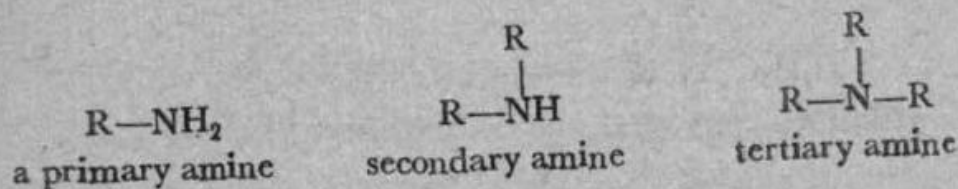


where R_1 and R_2 may be hydrogen atoms or any alkyl groups.

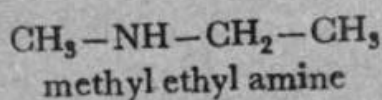
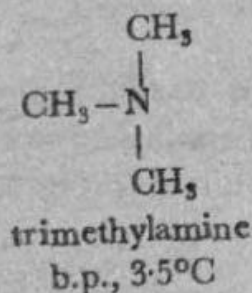
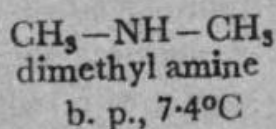
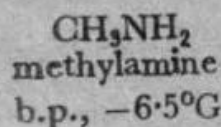
In summary alkyl halides may be used for synthesizing a large variety of organic compounds either through SN_2 or E2 reactions or by first changing them to Grignard reagents.

ALIPHATIC AMINES

Amines can be considered as alkyl derivatives of ammonia. Classification of amines is based on the number of alkyl groups attached to the nitrogen atom, e.g.

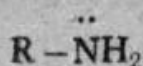


The R groups of secondary or tertiary amines may be same or different. For naming the compounds, the suffix—amine is added to the name of the alkyl group. The prefix di- or tri- is added before the name of the alkyl group when necessary, e.g.



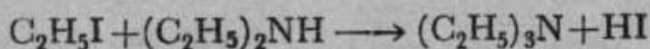
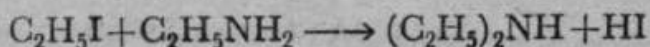
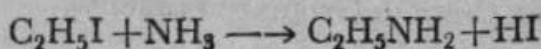
THE STRUCTURE OF AMINES

The nitrogen atom in an amine molecule is sp^3 hybridized. Three sp^3 orbitals of the nitrogen atom are partially filled and can overlap with the partially filled orbitals of other atoms to form NH_3 , NH_2R , NHR_2 or NR_3 . The fourth sp^3 orbital is filled with an electron pair and is not used in bond formation. Thus ammonia and alkyl amines have tetrahedral geometry (see Chapter 12). The unshared pair of electrons is shown with two dots on nitrogen in ordinary structural formulas :



GENERAL METHODS OF PREPARATION :

1. Interaction of ammonia and alkyl halides (Hofmann's method)



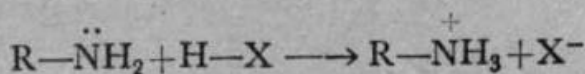
2. When vapours of alcohol are mixed with ammonia and passed over heated thoria :



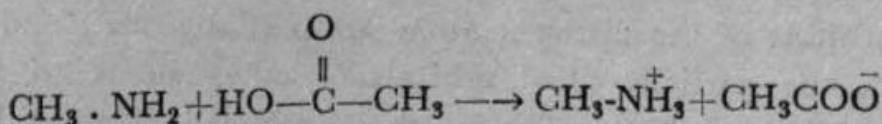
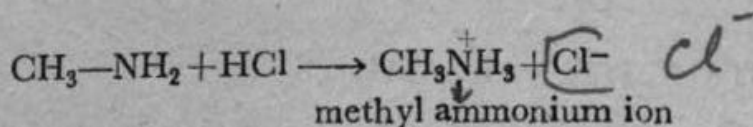
REACTIONS

The important reactions of amines are mainly due to the fact that the nitrogen atom can donate the unshared pair of electrons to an electrophilic centre to form a new bond. Examples are briefly discussed below :

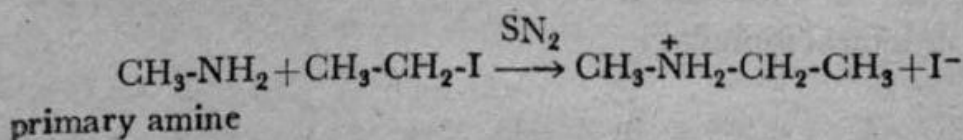
(1) **Basic Properties :** The most characteristic property of amines is their ability to act as bases by donating the unshared electron pair of the nitrogen atom to a proton when treated with acids.



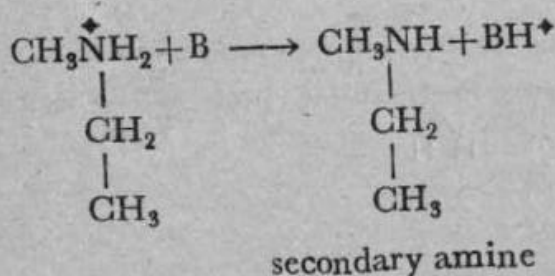
H—X may be an inorganic acid (*e.g.*, HCl, HBr, HI, H₂SO₄) or an organic acid such as CH₃COOH.



(2) **Alkylation :** Amines can act as nucleophiles in the S_N2 reactions of alkyl halides, *e.g.*

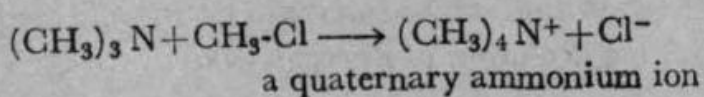
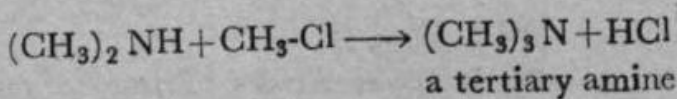
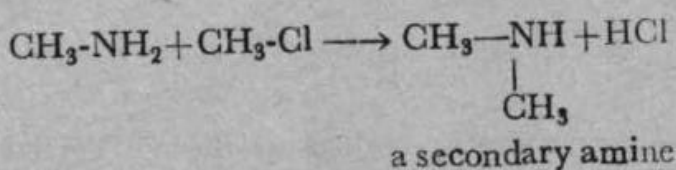
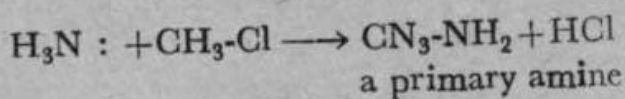


The initially formed methylethylammonium ion will react with **excess** of primary amine or with some other base and liberate the free secondary amine.



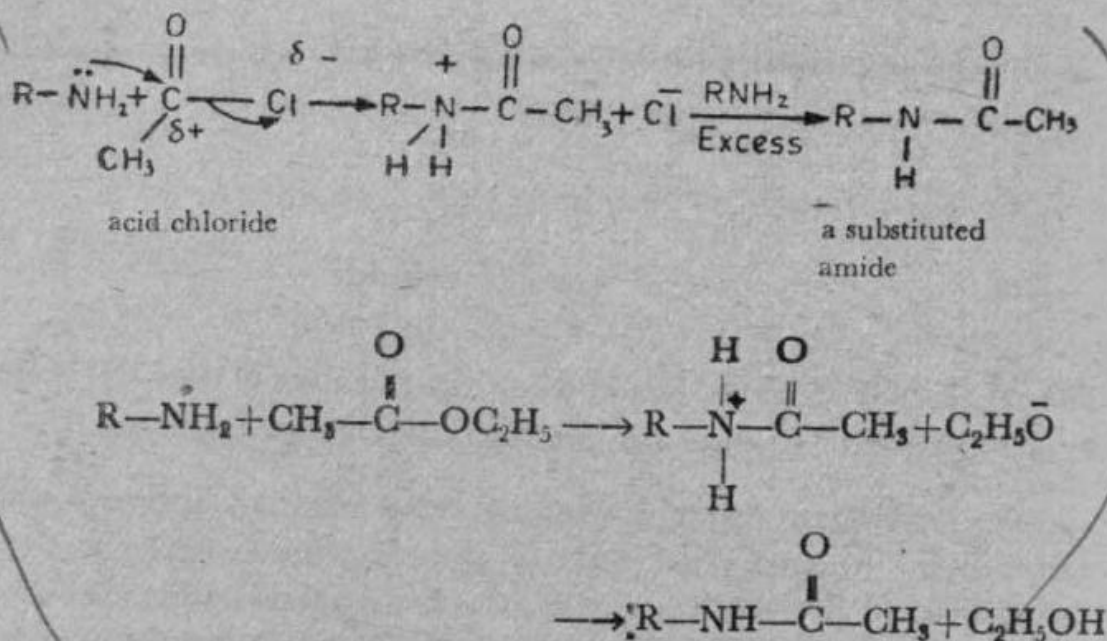
The net result is the replacement of a hydrogen atom of the —NH_2 group by an alkyl group. Hence the name *alkylation* for such reactions.

The alkylation reaction does not stop after a single alkylation step, because secondary and tertiary amines are also nucleophilic and will themselves give the $\text{S}_{\text{N}}2$ reactions with the alkyl halide. Therefore when ammonia is treated with an alkyl halide a **mixture** of several products is obtained.

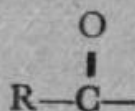


The second product of each reaction, the H—Cl molecule, is actually never formed in the reaction. The initially formed cation will react with excess NH_3 to form free amine and $\overset{+}{\text{N}}\text{H}_4\text{Cl}^-$ after each step. This reaction is useful in the preparation of amines even though a mixture of products results. The difference in the boiling points of the various amines present in the mixture is usually large enough to allow separation by fractional distillation, especially if the alkyl group of the alkyl halide is bigger than the methyl group.

(3) **Acylation :** Amines also react with acid chlorides and with esters by donation of the unshared electron pair of the nitrogen atom to the electrophilic carbon atom of the carbonyl group, *e.g.*,

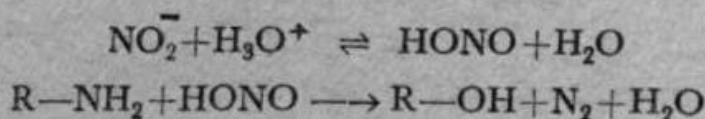


Reaction of an amine with an acid chloride or with an ester results in the replacement of one hydrogen atom of an amine by an acyl group.

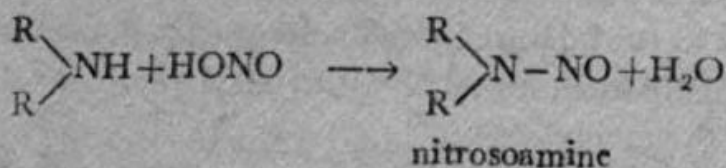


These reactions are therefore called *acylations*. Tertiary amines cannot be acylated.

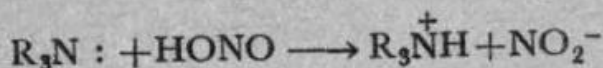
(4) **Reactions with Nitrous Acid :** Primary amines react with nitrous acid (a solution of sodium nitrite in acidified water) to form alcohols with the evolution of nitrogen gas.



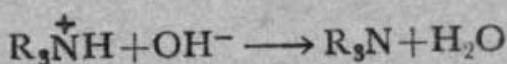
Secondary amines under the same conditions produce a water insoluble nitroso compound which separates out as a yellow oily liquid.



Tertiary amines do not react with nitrous acid to form alcohols or nitrosoamines. They simply accept a proton from the nitrous acid and form salts as with other acids.

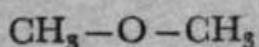


Thus the difference in the behaviour of primary, secondary and tertiary amines towards nitrous acid can be used to distinguish between these three types of amines. A primary amine gives an alcohol with the evolution of nitrogen gas, a secondary amine forms a water insoluble yellow oily nitroso compound and the tertiary amines form water soluble salts from which they can be regenerated by addition of alkali.



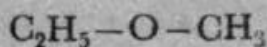
ETHERS

Organic compounds which contain an oxygen atom directly bonded to two carbon atoms (C—O—C) are called *ethers*, and may be represented by the general formula R—O—R' where R and R' are two alkyl groups which may be same or different. They are named by writing the word ether after the names of the two alkyl groups. When the two R groups are same the prefix di- is added before the name of the alkyl group. Examples are :



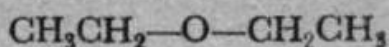
dimethyl ether

b.p., -24.9°C



methyl ethyl ether

b.p., 7.9°C



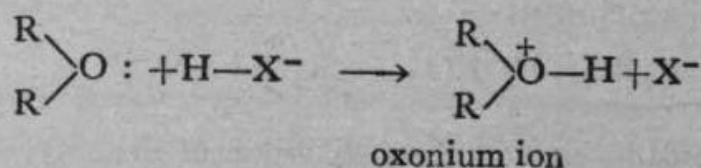
diethyl ether

b.p., 34.6°C

REACTIONS

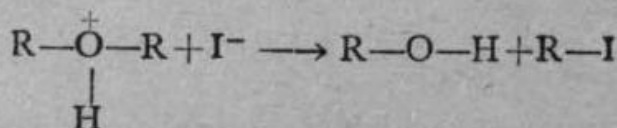
The ether linkage (C—O—C) is relatively unreactive. Because of their relatively inert nature and because they can dissolve many organic compounds, ethers are useful solvents for fats, oils, gums and many other organic materials. Recall the use of diethyl ether (usually simply referred to as ether) as solvent in the preparation of Grignard reagents.

The oxygen atom of an ether molecule contains unshared electron pairs and therefore can react with strong acids by accepting a proton to form an oxonium ion.

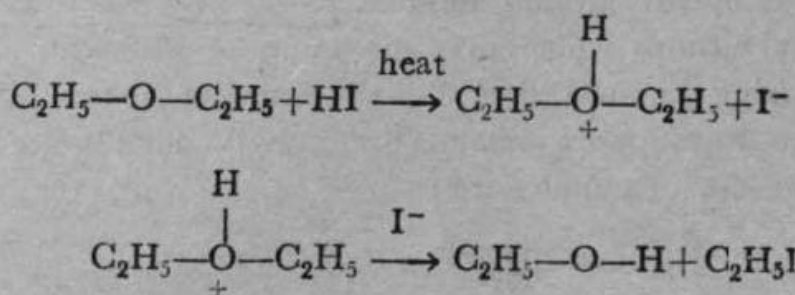


(A positively charged ion containing an oxygen atom bonded to three other groups is called an oxonium ion, e.g. H_3O^+ , $\text{R}-\text{O}^+ \begin{array}{c} \text{H} \\ \diagup \\ \diagdown \end{array} \text{H}$ etc.).

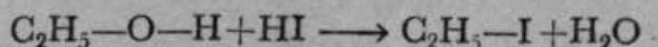
If the anion of the acid used (X^-) is a strong nucleophile, it reacts with the oxonium ion breaking an oxygen-carbon bond. For example if $\text{H}-\text{X}$ were $\text{H}-\text{I}$, then



Diethyl ether will react with $\text{H}-\text{I}$ as follows :



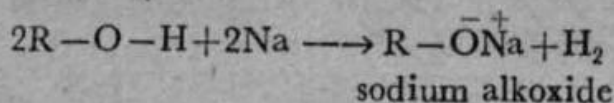
The alcohol, which is one of the products of reaction, reacts further with $\text{H}-\text{I}$ to form another alkyl iodide molecule under the conditions of the reaction.



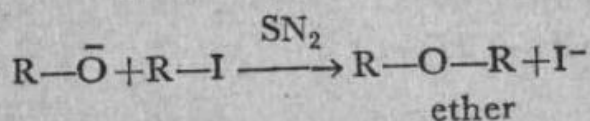
PREPARATION

Ethers are most commonly prepared from alcohols by the following two methods :

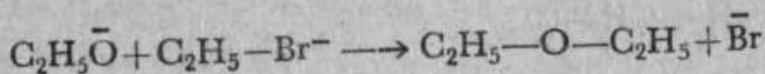
(1) An alcohol is reacted with metallic sodium to form what is known as an alkoxide ion



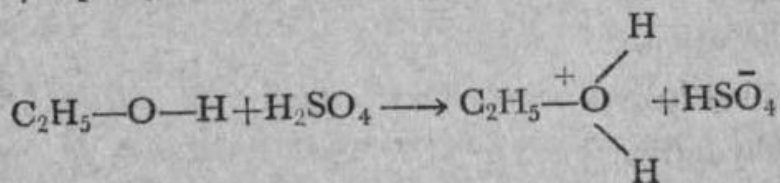
The alkoxide ion is a strong nucleophile and therefore reacts with alkyl halides in the SN_2 manner.



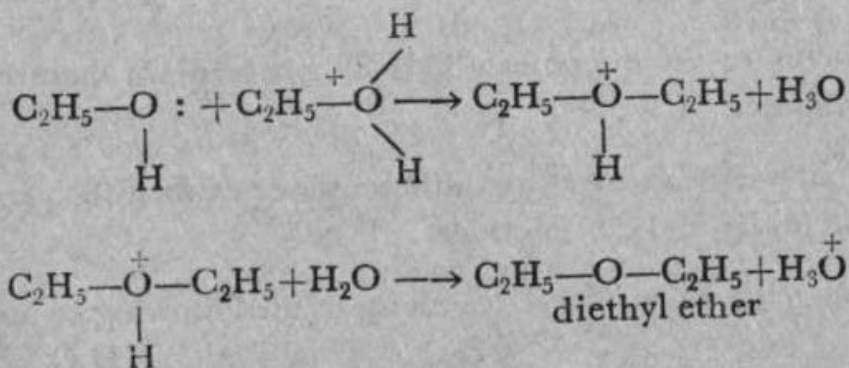
The two R groups can be same or different. This method of the preparation of ethers is called the *Williamson Synthesis*. Diethyl ether will be prepared by the Williamson method as follows :



2. In the second method an alcohol is treated with a strong acid (commonly H_2SO_4) to form an oxonium ion



The oxonium ion reacts with another alcohol molecule to give the ether.

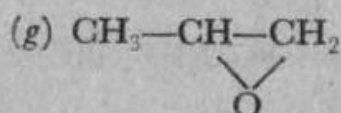
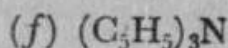
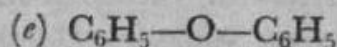
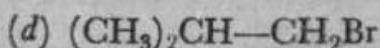
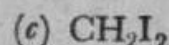
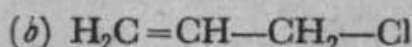
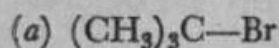


Questions

1. Write structural formulas for the following compounds :

- (a) 3-bromo-1-butene,
- (b) 2, 2-dibromopropane,
- (c) 1, 1, 2-trichloroethane,
- (d) tri-iodomethane,
- (e) ethyl-isopropyl ether,
- (f) dimethyl ethyl amine,
- (g) Quaternary methyl ammonium hydroxide.

2. Name the following compounds :



3. Define and illustrate with examples the following terms :

(a) alkylation,

(b) amination,

(c) dehydration,

(d) dehydrohalogenation,

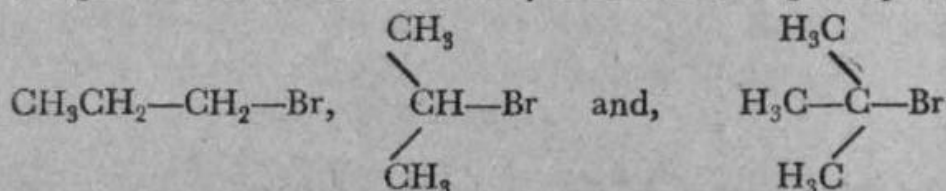
(e) hydrolysis,

(f) acylation.

4. There are three isomeric $\text{C}_4\text{H}_9\text{Br}$, write down their structural formulas.

5. What are the features that differentiate between ($\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$), and (b) $\text{E}1$ and $\text{E}2$ reactions.

6. Assign the order of $\text{S}_{\text{N}}1$ reactivity to the following compounds :



7. Write equations for the following reactions :

(a) 2-bromopropane with sodium ethoxide,

(b) 1-bromopropane with sodium ethoxide,

(c) methyl iodide with diethyl amine,

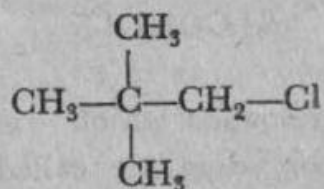
(d) sodium iodide with bromo-ethane,

(e) carbon dioxide with ethyl magnesium bromide,

(f) potassium cyanide with methyl iodide.

8. How many isomeric chloro-propanes are possible by addition of HCl to propene? Which is the most likely product and why?

9. Is it possible to get an alkene by treating



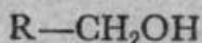
with sodium hydroxide?

10. Ethyl methyl ether may be prepared by heating a mixture of ethyl and methyl alcohols with H_2SO_4 . What other ethers might be simultaneously formed?
11. Isopropyl amine, methyl ethyl amine and tri-methyl amine are isomers, show how they can be distinguished by their reaction with HNO_2 ?
12. Quantitative chemical analysis of a mono-alkyl halide showed that it contained 70.3% chlorine. What is the smallest possible molecular weight that can be assigned to this compound? Suggest a molecular formula.
13. What volume of 0.5 N hydrochloric acid would be required to exactly neutralize 36.5g of diethyl amine? (Ans. 1 l)
-

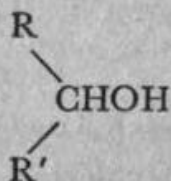
CHAPTER 15

ALCOHOLS

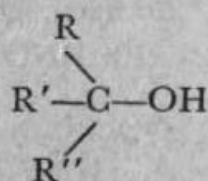
Aliphatic organic compounds which contain a hydroxy group, —OH , bonded to a carbon atom are called *monohydric* alcohols. A compound can have more than one hydroxyl groups in its molecule. Such compounds are called *polyhydric* alcohols. Compounds that have two hydroxyl groups on different carbon atoms are commonly known as *glycols*. Monohydric alcohols are classified as *primary*, *secondary*, or *tertiary*, depending upon whether the —OH group is bonded to a primary, a secondary, or a tertiary carbon atom.



primary alcohol



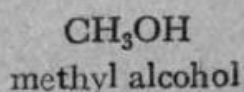
secondary alcohol



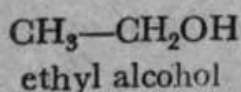
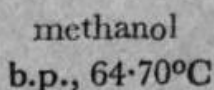
tertiary alcohol

Nomenclature : (1) Alcohols containing up to five carbon atoms are known by their common names. The word alcohol is written after the name of the alkyl group to which the —OH is bonded. The prefix, *sec-*, or *ter-* is added before the name of the alkyl group whenever necessary.

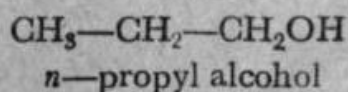
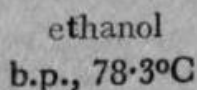
(2) The IUPAC System. The ending —e of the IUPAC name of the parent alkane is changed to —ol . The position of the —OH group is indicated by a number before the modified name. The carbon chain containing the hydroxy group is numbered, beginning from that end which would assign the lowest possible number to the carbon atom linked to the —OH group. The common and the IUPAC names of a few alcohols are given below :



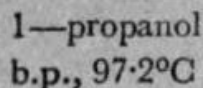
or

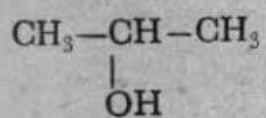


or



or

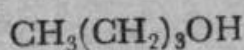


*sec*-propyl alcohol

or

2—propanol

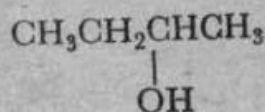
b.p., 82.30°C

*n*-butyl alcohol

or

1—butanol

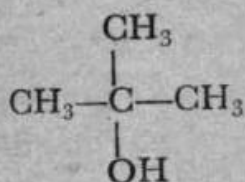
b.p., 117.7°C

*sec*-butyl alcohol

or

2—butanol

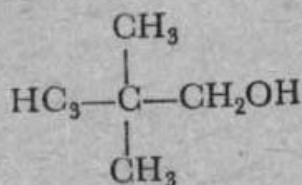
b.p., 99.5°C

*ter*-butyl alcohol

or

2—methyl—2—propanol

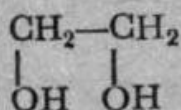
b.p., 82.5°C



neopentyl alcohol

or

2, 2—dimethyl—1—propanol

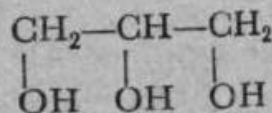


ethylene glycol

or

1, 2—ethanediol

b.p., 197°C



glycerol

or

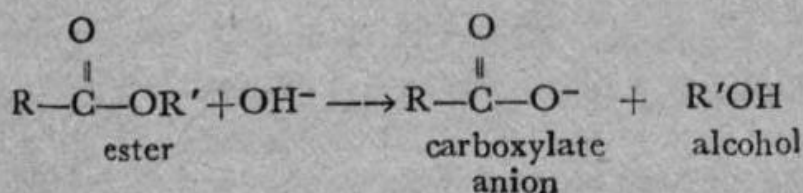
1, 2, 3—propanetriol

b.p., 290°C

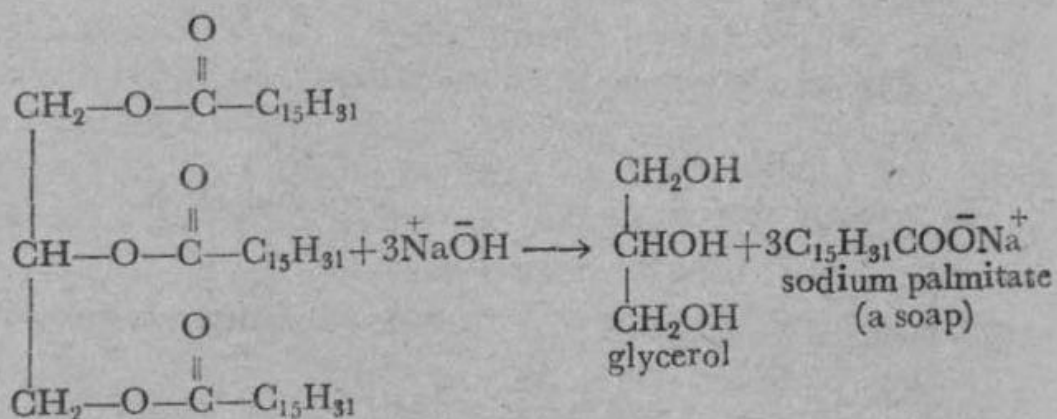
Polyhydric alcohols having more than one —OH group on a single carbon atom are rare, because they break down readily to form a carbonyl compound.

Preparation : Although alcohols can be prepared by a number of methods, only the more commonly used methods will be described here.

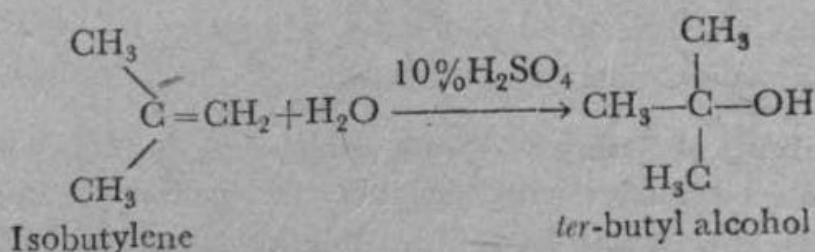
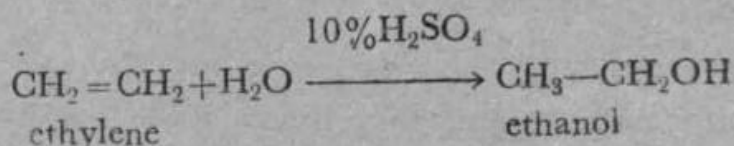
(1) **Hydrolysis of Esters :** Esters, which can be made by the reaction of carboxylic acids with alcohols, are hydrolysed into acid and alcohol by treatment with an aqueous solution of sodium hydroxide or potassium hydroxide, *e.g.*,



The method is of interest in the preparation of carboxylic acids as well as alcohols, especially from naturally occurring esters. For example, fats and oils are the esters of the trihydric alcohol glycerol with long chain carboxylic acids. Their hydrolysis with aqueous sodium hydroxide, called *saponification*, yields glycerol and the sodium salts of higher fatty acids. The sodium salts of higher fatty acids are used as *soaps*.

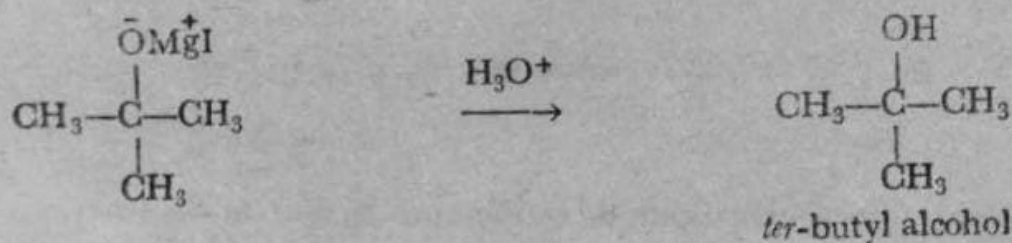
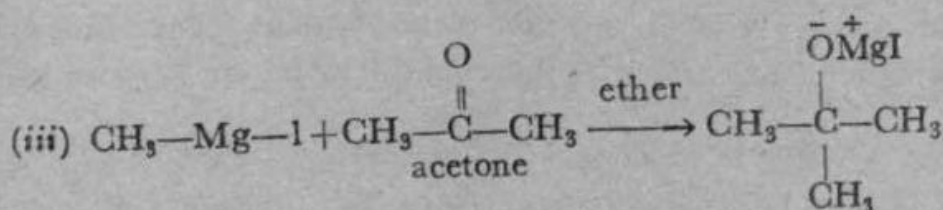
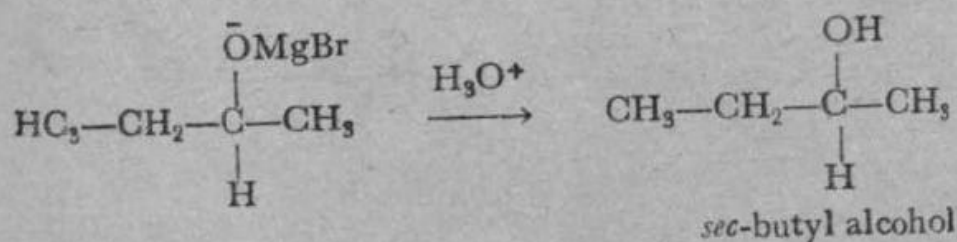
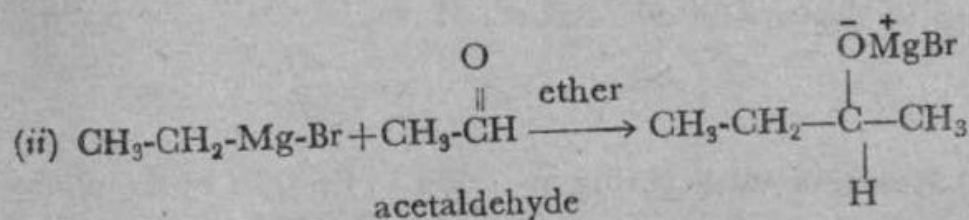
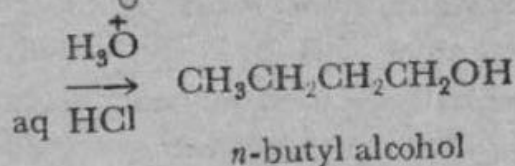
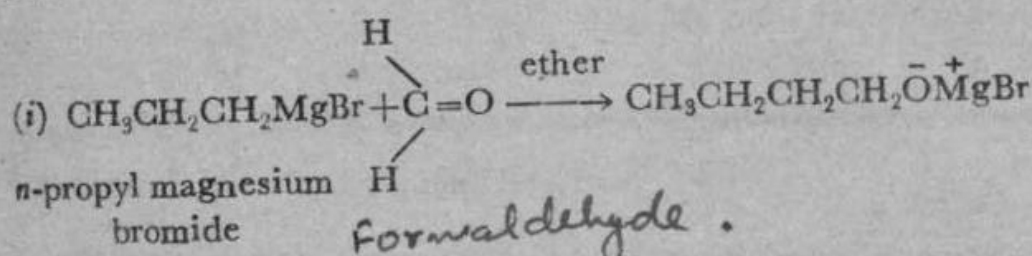


(2) **Hydration of Alkenes**: Alkenes react with water in the presence of an acid to form alcohols. The addition of water to alkenes (hydration) is of particular importance in the preparation of a number of commercially important alcohols. Thus ethanol and *ter*-butyl alcohol are prepared on a commercial scale by the hydration of the corresponding alkenes (see Chapter 13).



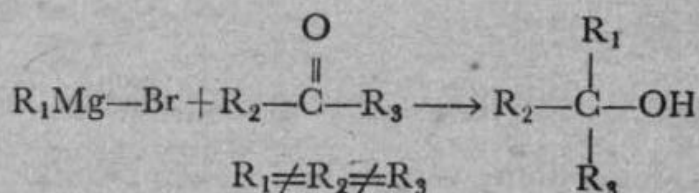
(3) **Reaction of Grignard Reagents with Carbonyl Compounds**: As shown in Chapter 14, Grignard reagents react with carbonyl compounds to form alcohols. Primary alcohols are formed when the carbonyl compound is formaldehyde, CH_2O , secondary alcohols when the carbonyl compound is an aldehyde other than

formaldehyde, and tertiary alcohols when the carbonyl compound is a ketone.

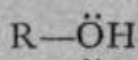


HCl is almost completely ionized in dilute aqueous solutions as follows $\text{HCl} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{Cl}^-$. Thus aqueous solution of strong acids such as HCl or H_2SO_4 are symbolized as H_3O^+ .

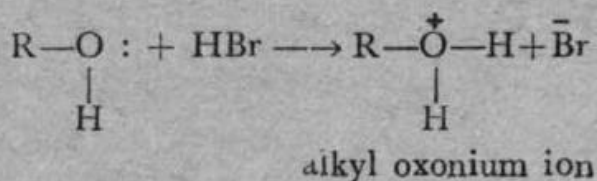
This method of preparation is particularly of value in making tertiary alcohols in which all the three R groups are different.



Structure and Reactions : The oxygen atom in alcohols, like the oxygen atom of H_2O , is sp^3 hybridized (see Chapter 12). Two of the sp^3 orbitals are used in bond making with a hydrogen and a carbon atom. The remaining two sp^3 orbitals are filled with an electron pair each. Thus the oxygen atom in alcohols has two unshared pairs of electrons, as shown with dots below :



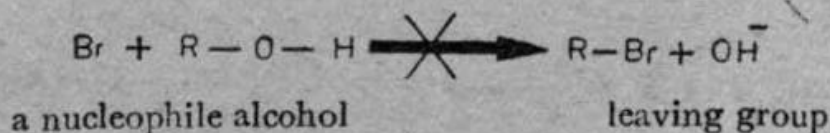
(1) Reaction with Halogen Acids : Because of the presence of unshared electron pairs on their oxygen atom, alcohols act as bases towards strong acids.



The C—O bond in the alkyl oxonium ion is highly polarized, creating a partial positive charge on the carbon atom. The electrophilic carbon will therefore react with nucleophiles giving an S_N reaction *e.g.*,



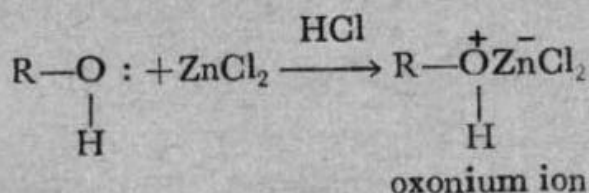
The C—O bond in the alcohol molecule is much less polarized. The following reaction, therefore, does not take place :



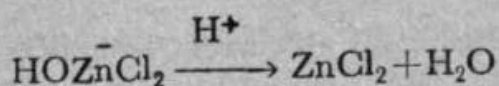
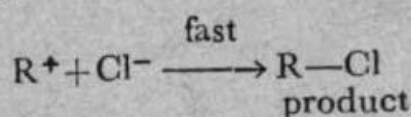
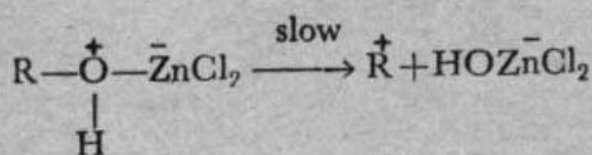
Another way of explaining this difference is that in S_N reactions H_2O is a good leaving group, but OH^- is a very poor leaving group. Other halogen acids react similarly. The order of reactivities of the halogen acids is $\text{HI} > \text{HBr} > \text{HCl}$. With a given halogen acid a tertiary alcohol reacts most rapidly and a primary alcohol reacts

most slowly. The reactivity of secondary alcohols is in the middle, *i.e.* the order of reactivities is tertiary > secondary > primary. In fact primary alcohols (least reactive) react with the least reactive halogen acid, H—Cl, only in the presence of a catalyst, ZnCl₂.

Alcohols react with a solution of ZnCl₂ in concentrated hydrochloric acid to form an oxonium ion in the first place.

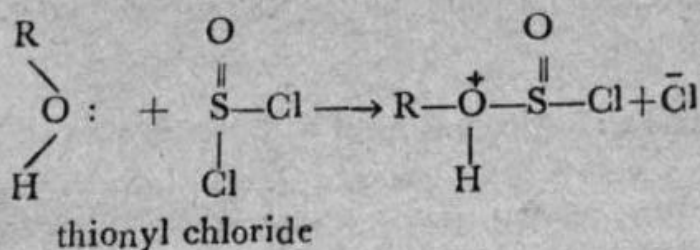


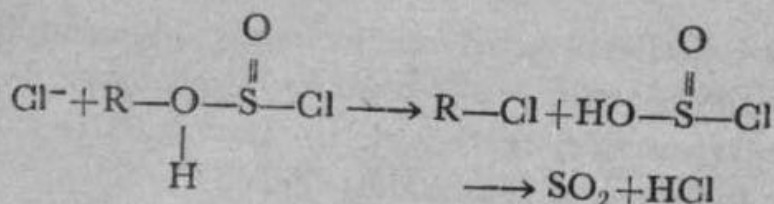
The oxonium ion then reacts by S_N1 mechanism as follows :



The slow step of the reaction is the formation of R⁺, a carbonium ion. Because a tertiary carbonium ion is more stable than a primary carbonium ion, tertiary alcohols would form an alkyl halide most rapidly and primary alcohols would do so most slowly. This reaction is therefore used as a test for distinguishing primary, secondary, and tertiary alcohols, and is called the *Lucas test*. In this test ZnCl₂ is dissolved in concentrated acid and an alcohol added to the solution. A tertiary alcohol will form an insoluble layer of a tertiary alkyl halide *immediately* on mixing, a secondary alcohol will form a secondary alkyl halide in 5 to 10 minutes, and a primary alcohol will react only on heating to give the insoluble primary alkyl halide.

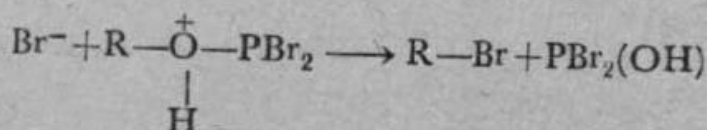
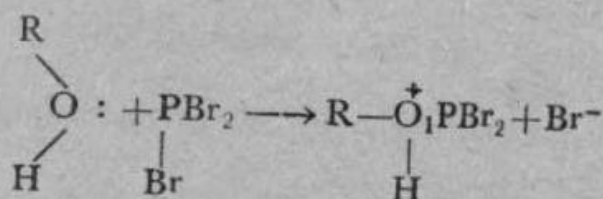
Alkyl halides are better prepared by the reaction of inorganic acid halides with alcohols, *e.g.*



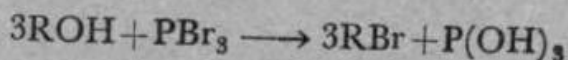


The net result is the replacement of the $-\text{OH}$ group of the alcohol by a chlorine atom.

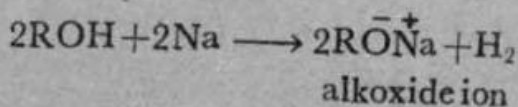
Similarly halides of phosphorus replace the $-\text{OH}$ by a halogen atom.



The reaction of PBr_3 and PI_3 with alcohols is one of the best methods for making alkyl bromides and alkyl iodides :



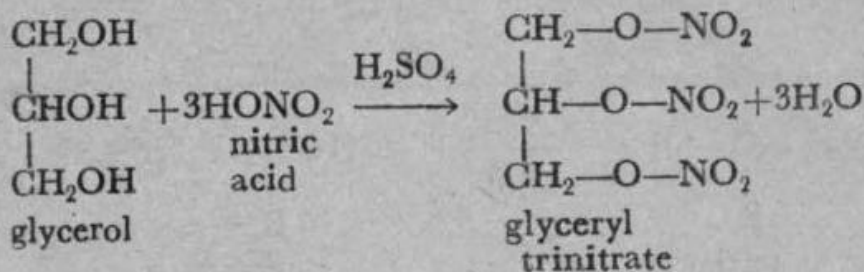
(2) **Reaction with Metals :** Since the $\text{O}-\text{H}$ bond in alcohols is partially ionic due to the difference in the electronegativities of oxygen and hydrogen atoms, alcohols react with metals such as sodium to form alkoxides.



The alkoxide ion is a stronger base and a stronger nucleophile than the parent alcohol. Hence it is used in the Williamson synthesis of ethers. $\text{CH}_3\overset{-}{\text{O}}\overset{+}{\text{Na}}$ and $\text{C}_2\text{H}_5\overset{-}{\text{O}}\overset{+}{\text{Na}}$ are called sodium methoxide and sodium ethoxide respectively.

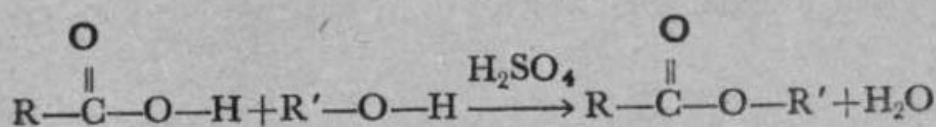
(3) **Ester Formation :** Alcohols react with inorganic as well as organic acids to form *esters* and water. Alkyl halides may be regarded as esters of halogen acids with alcohols. Glycerol, a trihydric

alcohol, reacts with nitric acid in the presence of sulphuric acid to form a triester.

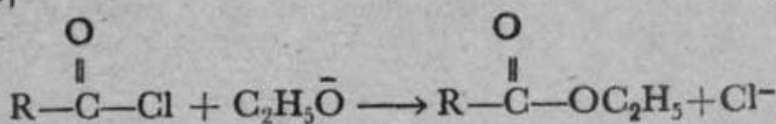


Glyceryl trinitrate, commonly called “nitroglycerine”, is highly explosive. Its mixture with fine sand forms the well known explosive *dynamite*.

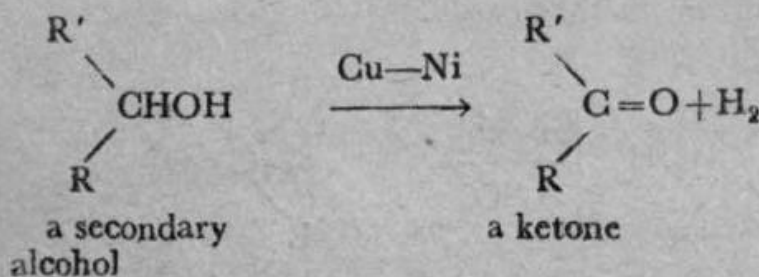
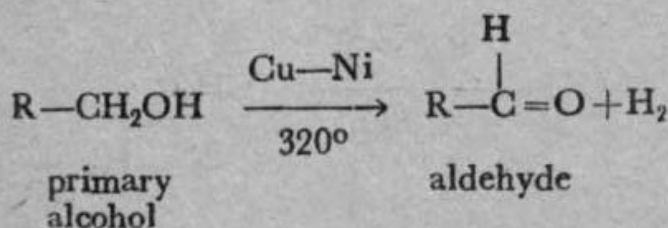
Organic esters are formed by the reaction of a carboxylic acid with an alcohol in the presence of an acid catalyst.



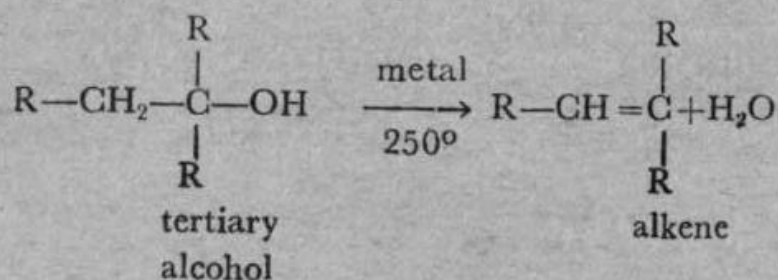
A good method of making esters is to treat an acid chloride with an alkoxide ion.



(4) Dehydrogenation : Alcohols are dehydrogenated when their vapours are passed over a heated metal catalyst. Primary alcohols are dehydrogenated into aldehydes and secondary alcohols to ketones.

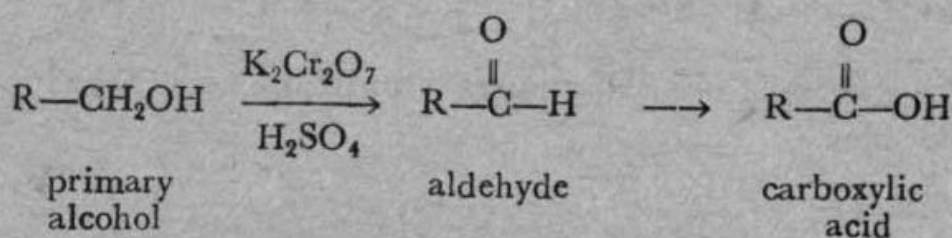


Tertiary alcohols do not undergo dehydrogenation because they have no hydrogen atom on the carbon atom carrying the —OH group, at higher temperatures they may be dehydrated.

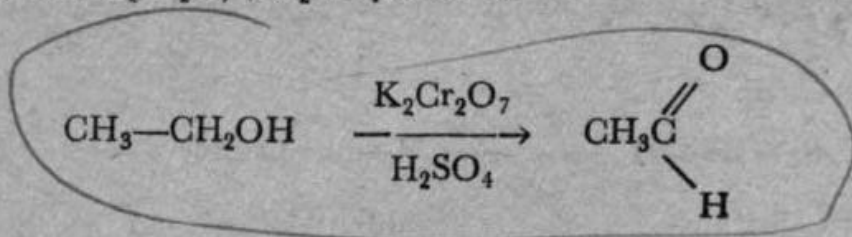


Note that dehydrogenation means removal of a hydrogen molecule whereas dehydration means removal of a molecule of water.

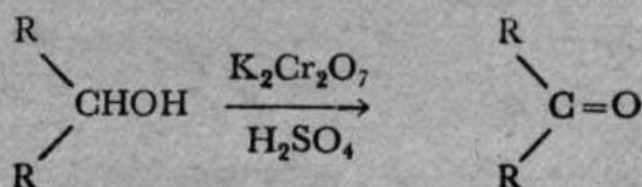
(5) **Oxidation :** Alcohols are oxidized by oxidizing agents such as $\text{K}_2\text{Cr}_2\text{O}_7$ and H_2SO_4 , and alkaline KMnO_4 . Primary alcohols are first oxidized to aldehydes which are in turn oxidized to carboxylic acids.



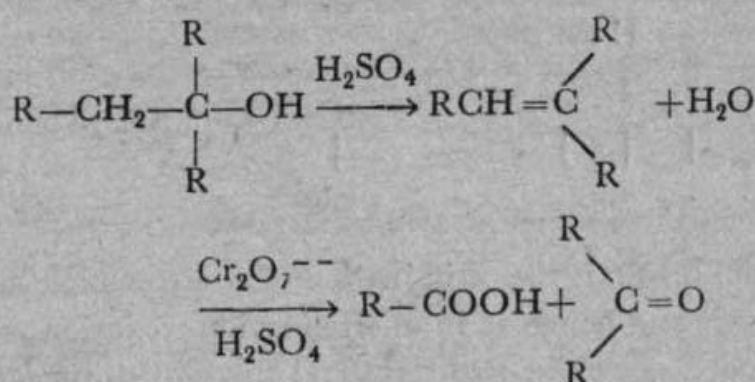
The reaction can be used to prepare aldehydes which have low boiling points, the aldehyde being distilled off as soon as it is formed. Thus acetaldehyde (boiling point 21°C) is made from ethanol by treatment with $\text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4$ at 50°C .



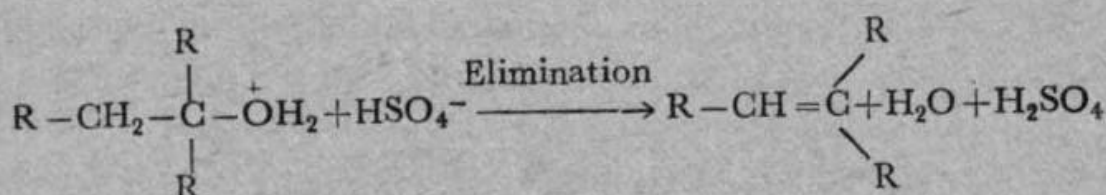
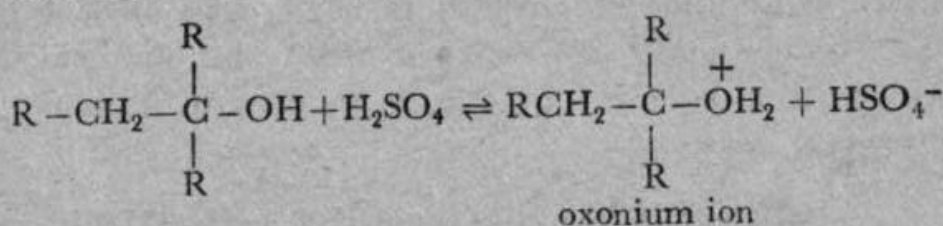
under similar conditions secondary alcohols are oxidized to ketones, which are not oxidized further easily.



Of the three types of alcohols tertiary alcohols are the most difficult to oxidize. They are not oxidized by neutral or alkaline KMnO_4 . In acidic dichromate they first form an alkene which is then oxidized to a carbonyl compound and an acid.

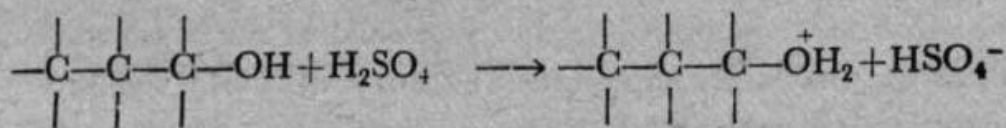


Note that the first step involves elimination of H_2O from the alcohol under the influence of acid catalyst.

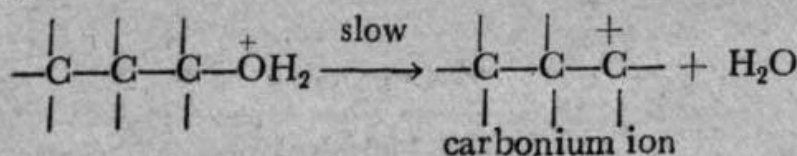


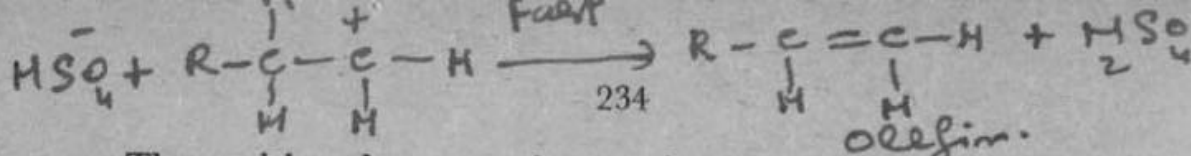
Also note that each of the two final products of the oxidation of a tertiary alcohol has fewer carbon atoms in the molecule than the parent alcohol. This means that a $\text{C}-\text{C}$ bond is broken during the oxidation.

(6) **Dehydration to Alkenes:** Alcohols form oxonium ions when treated with acids, as shown earlier.

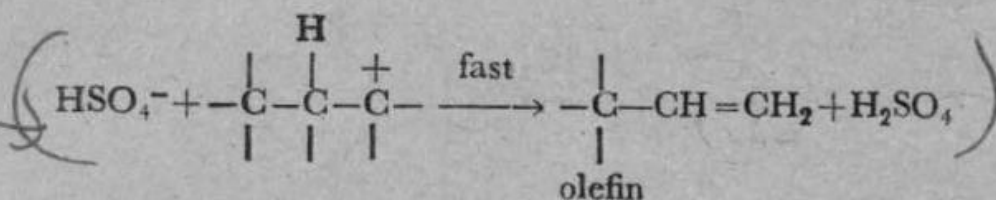


The $\text{C}-\text{O}$ bond in the oxonium ion breaks to form a carbonium ion and water.

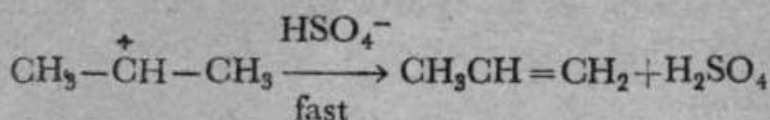
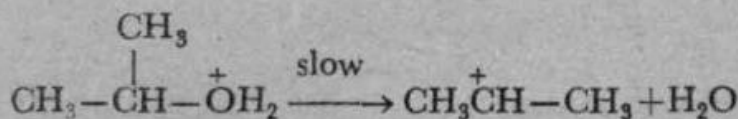
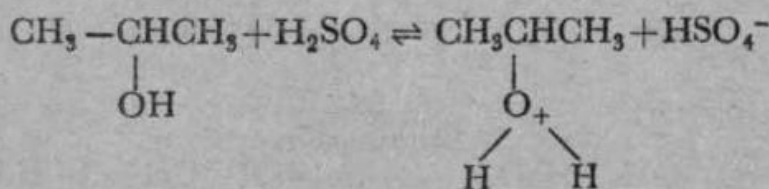




The positive charge on the α carbon atom makes the β hydrogen atoms acidic for the same reason that were given in the case of E2 reactions of alkyl halides. The carbonium will, therefore react with a base (HSO_4^-) and lose a β -H to form an olefin.

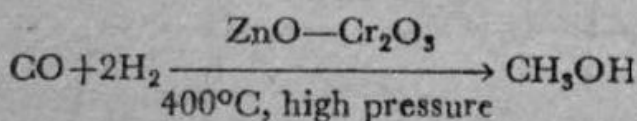


The net result is the elimination of a water molecule from the alcohol molecule and hence it is an elimination reaction. Since in this case, the reaction occurs in two steps and the first unimolecular step is slow and rate determining, the overall reaction is called a *unimolecular elimination* or E1 reaction, where 1 stands for unimolecular. E1 acid catalysed dehydration of alcohols is not a good method for making alkenes, because many side reactions occur. E2 eliminations of alkyl halides with a base are practically better. An example of an E1 reaction is :



SIMPLE ALCOHOLS

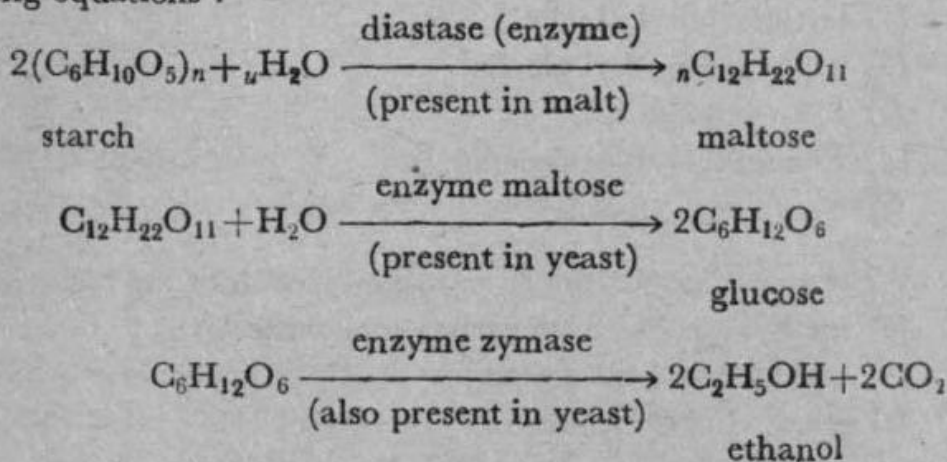
Methanol, is obtained by heating wood in the absence of air until it has thermally decomposed. The tarry distillate contains sufficient quantities of methanol and hence the name "wood-spirit". Now-a-days methanol is increasingly produced by the catalytic reduction of carbon monoxide.



Methanol is largely used as a solvent, and in the manufacture of formaldehyde. Methanol is very poisonous and may cause blindness and even death. It is therefore used as a denaturant for ethanol.

Ethanol : Since ages, ethanol has been obtained by the fermentation of sugar solution or grain starch. Fermentation is a biochemical process brought about by *enzymes* in yeast or other micro-organisms. These enzymes are complex organic catalysts, and possess a specific action.

The fermentation processes leading to ethanol are shown by the following equations :

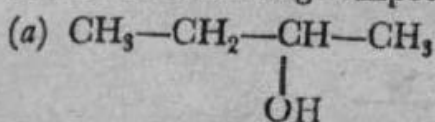


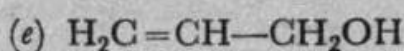
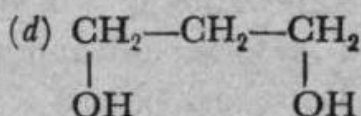
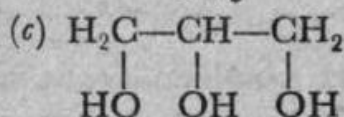
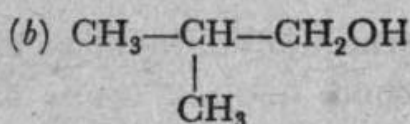
Fermentation yields a solution containing about 12% ethanol. 95% ethanol (called *rectified spirit*) is obtained by fractional distillation of the fermented solution. Completely anhydrous ethanol (*absolute alcohol*) is obtained by shaking the 95% ethanol with calcium oxide, which absorbs moisture, and distilling the alcohol. Ethanol is rendered unfit for drinking by addition of poisonous substances such as methanol. The process is called *denaturing of alcohol*. When ethanol has been denatured by adding methanol, it is called *methylated spirit*.

Alcohol, when used as a beverage, is heavily taxed in all countries. However, when used as a solvent or a starting material for other chemicals, it is sold tax-free. In order to avoid illegal use of tax-free alcohol for drinking purposes, the alcohol meant for commercial purposes is denatured.

Questions

1. Name the following compounds :





2. Write structural formulas for the following compounds :

- (a) tertiary butyl alcohol,
- (b) triphenyl methyl alcohol,
- (c) 1, 2—butanediol,
- (d) 2—methyl—1—propanol,
- (e) 2—butene—1—ol.

3. Write equations for the preparation of each of the following :

- (a) methyl alcohol from carbon monoxide,
- (b) ethyl alcohol from ethene,
- (c) ethanediol from ethene,
- (d) propene from *n*—propyl alcohol.

4. Write down the structural formulas of the three isomeric alcohols having the formula $\text{C}_4\text{H}_9\text{OH}$.

5. Show by means of equations the reactions which occur when the following reagents react with (i) water and (ii) methyl alcohol :

- (a) sodium,
- (b) PBr_3 ,
- (c) PCl_5 ,
- (d) thionyl chloride.

6. Define and illustrate with examples the following terms :

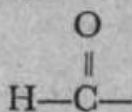
- (a) oxonium ion,
- (b) β —elimination,
- (c) dehydrogenation.

7. Describe the Lucas test for primary, secondary and tertiary alcohols.

CHAPTER 16

ALDEHYDES AND KETONES

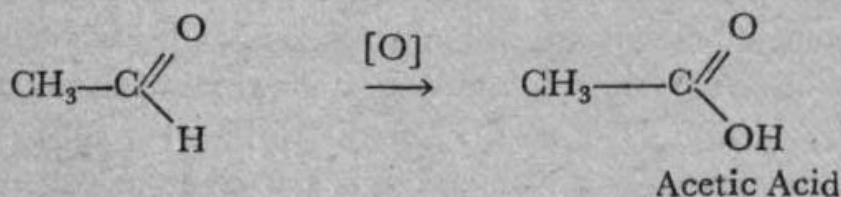
Organic compounds containing the carbonyl group >C=O , are called *Aldehydes* and *Ketones*. In aldehydes, the carbon atom of the carbonyl group is directly bonded to at least one hydrogen atom. Thus all aldehydes have the group



present in their molecule. Ketones are those compounds in which the carbonyl carbon atom is bonded to two other carbon atoms.

NOMENCLATURE

(1) **Common Names of Aldehydes :** The common names of aldehydes are derived from the common names of acids to which the aldehydes are oxidized. The ending *ic acid* of the acid is replaced by the word *aldehyde*. The position of substituents on the carbon chain is shown by Greek letters (α , β , γ , δ , etc.) the carbon atom adjacent to the carbonyl group being designated as α carbon. Thus the compound CH_3CHO on oxidation gives acetic acid.



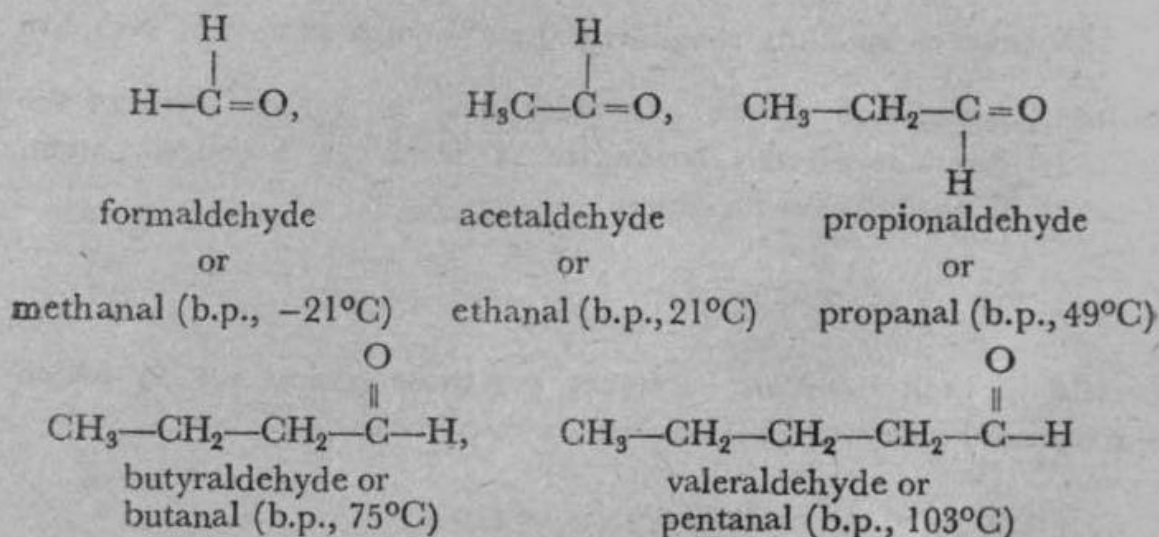
Therefore CH_3CHO is called acetaldehyde. Similarly

$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}-\text{C}-\text{H} \end{array}$ is called formaldehyde, because on oxidation it gives formic acid, $\begin{array}{c} \text{O} \\ \parallel \\ \text{H}-\text{C}-\text{OH} \end{array}$.

(2) **The IUPAC Names of Aldehydes :** The ending-*e* of the name of the alkane containing the same number of carbon atoms as the longest continuous chain containing the aldehyde group is

replaced by the ending-*al*. The positions of other groups on the chain are indicated by numbers. Numbering starts from the carbonyl carbon.

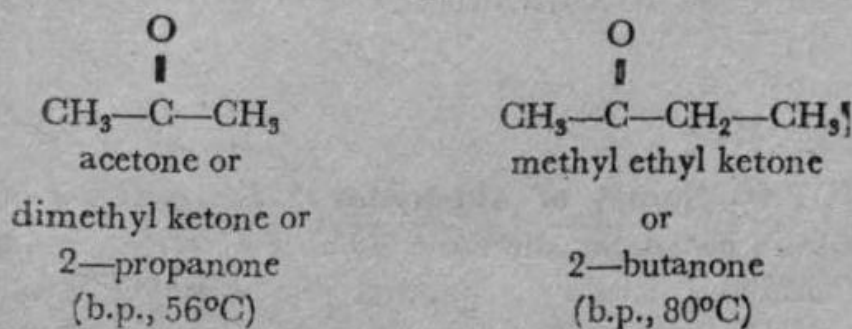
The common and the IUPAC names of a few aldehydes are given below. The boiling point of each aldehyde is indicated below the name :

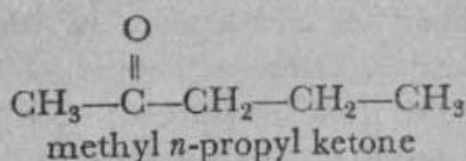


(3) **Common Names of Ketones :** The common names of ketones are obtained by writing the names of the alkyl groups to which the carbonyl carbon is bonded. The word ketone is then added as of separate word. The name of the lower alkyl group is written first. When the two alkyl groups are same, the prefix di— is added before the name of the alkyl group.

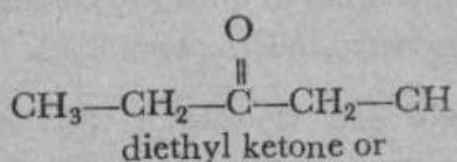
(4) **The IUPAC Names of Ketones :** The ending-*e* is dropped from the name of the alkane and suffix—*one* is added having the same number of carbon atoms as the longest continuous chain containing the carbonyl group. The position of the carbonyl group in the chain is indicated by a number. Numbering is started from that end which is nearest to the carbonyl group.

The common and the IUPAC names of a few ketones are given below, along with their boiling points.

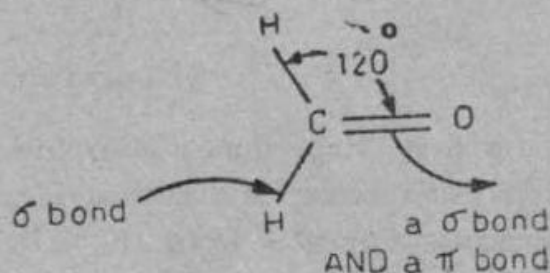




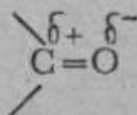
or

2—pentanone (b.p., 102°C)3—pentanone (b.p., 103°C)

Structure and Reactivity : The carbon atom of the carbonyl group (in aldehydes as well as ketones) is sp^2 hybridized. The three sp^2 hybrid orbital are used for making σ bonds with an oxygen atom and two other atoms (both carbon, both hydrogen, or one hydrogen and one carbon). The partially filled unhybridized p orbital of the carbonyl carbon atom and a partially filled p -orbital of the oxygen atom overlap to form a π bond. Thus there is a σ bond and a π bond between the carbonyl carbon and oxygen.



Since the oxygen atom is more electronegative than the carbon atoms, the π electrons are attracted more to the oxygen atom. The π bond is thus partially ionic as shown :

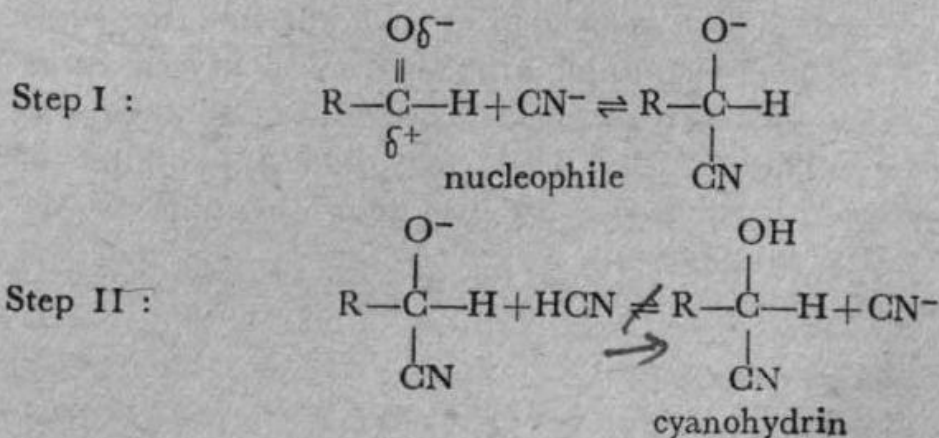


The carbonyl carbon atom has a partial positive charge on it and is electrophilic, whereas the oxygen atom bears a partial negative charge and is nucleophilic. Most of the reactions of aldehydes and ketones are initiated by the attack of a nucleophile on the electrophilic carbon, or by the attack of an electrophile on the nucleophilic oxygen. Note that the carbon-carbon double bond is not polarized, which accounts for the difference in the reactivities of an alkene double bond and a carbonyl double bond.

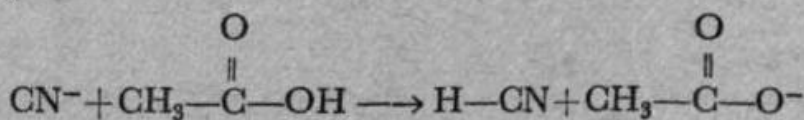
The properties of aldehydes and ketones in which the carbonyl group is involved are similar. However, some of the reactions of aldehydes are different from those of ketones, because the aldehydes have a hydrogen atom bonded to the carbonyl group.

(1) **Reaction with Grignard Reagents :** Aldehydes and ketones react with alkyl magnesium halides to form the corresponding alcohols. The reactions have been discussed in Chapter 15.

(2) **Addition of Hydrogen Cyanide :** Aldehydes and ketones react with HCN to form cyanohydrins. The reaction occurs by the nucleophilic attack of the cyanide ion on the electrophilic carbon atom of the carbonyl group.



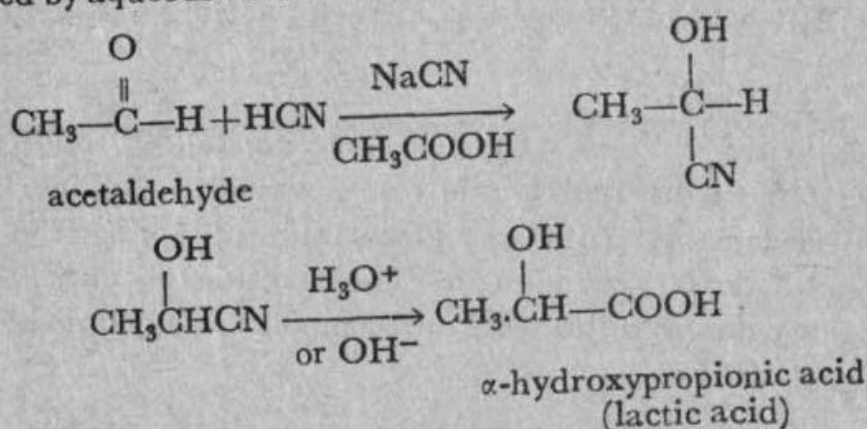
Note that, in the first step, the nucleophilic attack of the cyanide ion (CN^-) on the electrophilic carbonyl carbon atom gives an ion. This ion accepts a proton from HCN in the second step forming a cyanohydrin and regenerating the cyanide ion. Cyanide ion is, therefore, needed in small amounts. The reaction is carried out by adding an acid to a mixture of sodium cyanide and the carbonyl compound. The acid generates HCN from sodium cyanide during the reaction, *e.g.*



However, the quantity of acid added should be so controlled that it is not enough to convert all the cyanide ions into $\text{H}-\text{CN}$, because CN^- is a catalyst for the reaction.

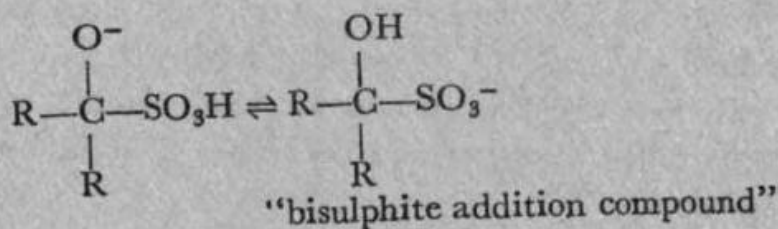
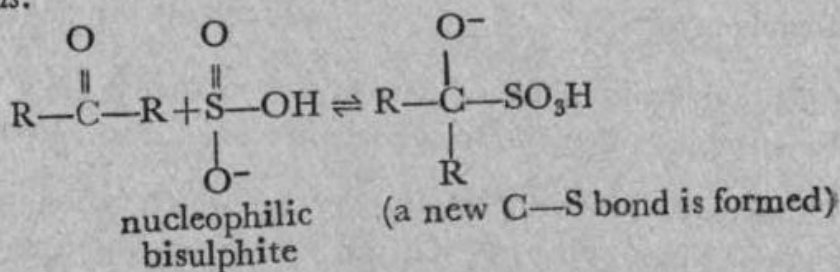
Although both the steps involved in cyanohydrin formation are reversible, the equilibria lie far to the right with most of carbonyl compounds, giving high yields of cyanohydrins at equilibrium.

Cyanohydrin formation is of interest, because the —CN group is hydrolyzed by aqueous acid or alkali into a carboxyl group.

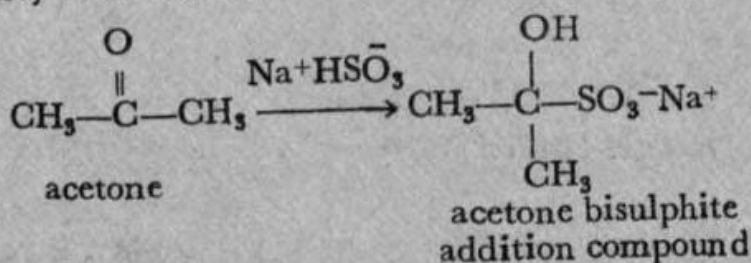


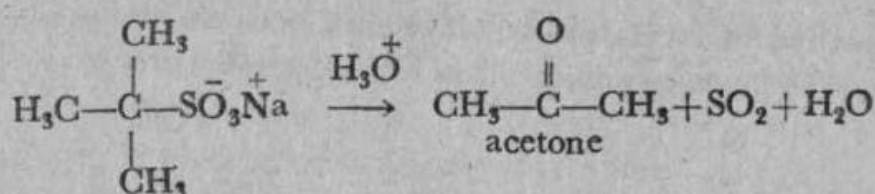
Thus the net result is the conversion of a carbonyl compound into an α -hydroxy acid containing one carbon atom more than the starting aldehyde or ketone.

(3) **Addition of Sodium Bisulphite** : Aldehydes and methyl ketones (in which at least one R is CH_3) react with a saturated aqueous solution of sodium bisulphite to form what are known as *bisulphite addition compounds*.



The bisulphite addition compounds when treated with aqueous mineral acids (H—Cl or H_2SO_4) break down into the carbonyl compound from which they were formed.

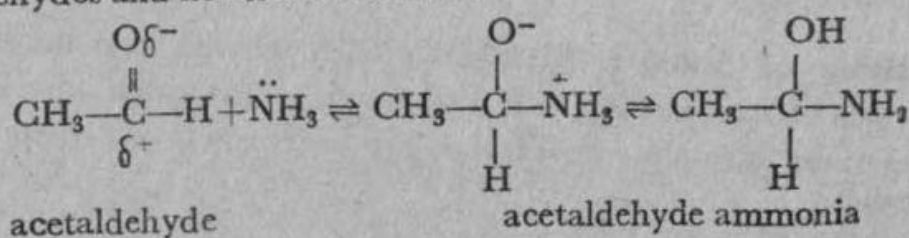




The bisulphite addition compounds are crystalline solids. They are separated from the reaction mixture, washed with an organic solvent and then treated with an aqueous mineral acid. The parent ketone or aldehyde is regenerated. The reaction is thus useful in separating aldehydes from those organic compounds which do not react with sodium bisulphite.

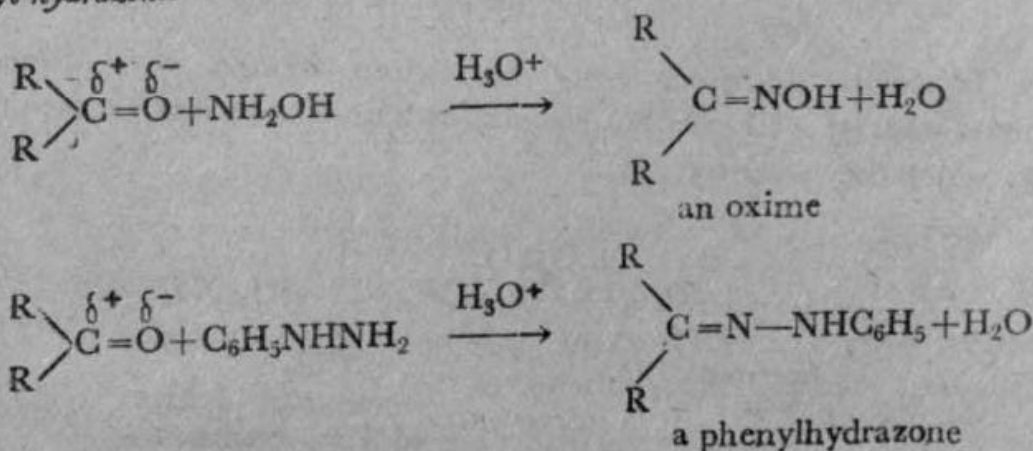
Ketones in which both alkyl groups are larger than methyl do not react with sodium bisulphite.

(4) Addition of Ammonia : Ammonia, a nucleophile reacts with aldehydes and ketones as follows :

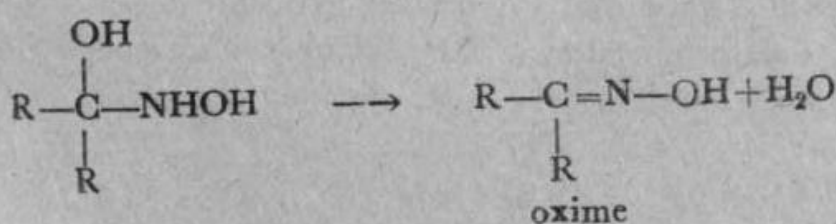
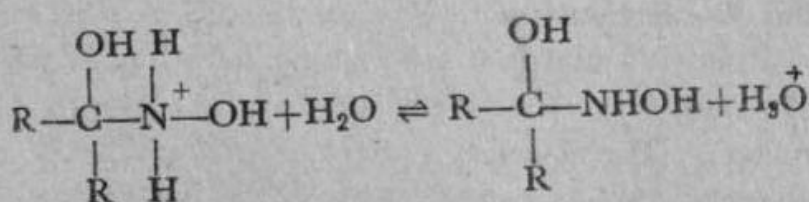
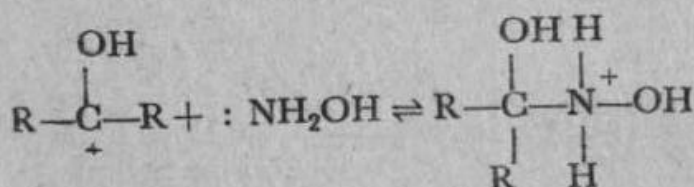
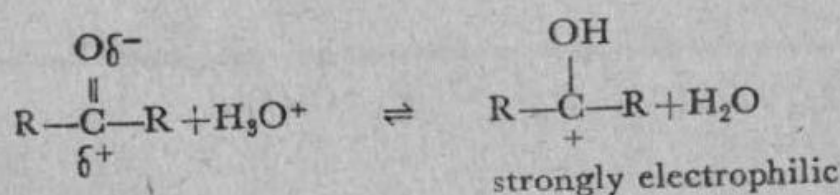


Addition compounds of carbonyl compounds with ammonia are usually unstable. They undergo dehydration and then polymerization.

There are, however, other reagents which also are nucleophilic due to an unshared electron pair on a nitrogen atom and which form stable products with aldehydes and ketones. Two such reagents are hydroxylamine ($:\text{NH}_2\text{OH}$) and phenylhydrazine ($\text{C}_6\text{H}_5\text{NH.NH}_2$). These reactions are acid catalyzed. The product of reaction with NH_2OH is called an *oxime* and that with phenylhydrazine is called a *phenyl-hydrazone*.

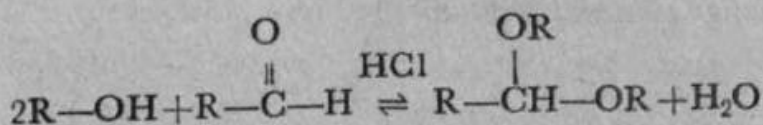


The final products, oximes or phenylhydrazones, of these reactions are formed after many complex intermediate steps. A simplified picture of the course of these reactions is given below :



Oximes and phenylhydrazones are usually crystalline solids with characteristic melting points. They are useful in identifying aldehydes and ketones.

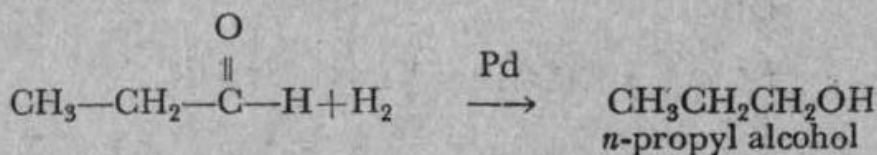
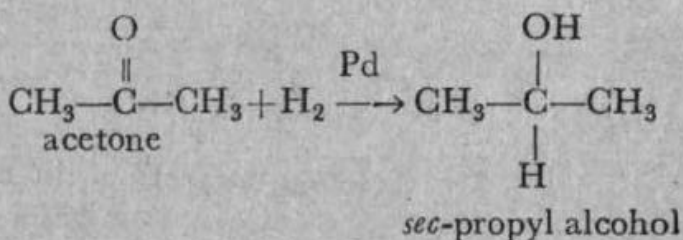
(5) Reaction with Alcohols : Alcohols react with aldehydes in the presence of dry $\text{H}-\text{Cl}$ as a catalyst to form *acetals*.



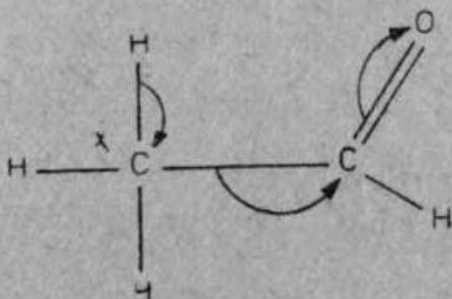
Since the reaction is reversible, excess of alcohol is used to drive the reaction to the right. Ketones do not give the corresponding reaction with alcohols readily.

The principle of acetal formation is similar to that explained for oxime formation. Acetals are stable in basic conditions.

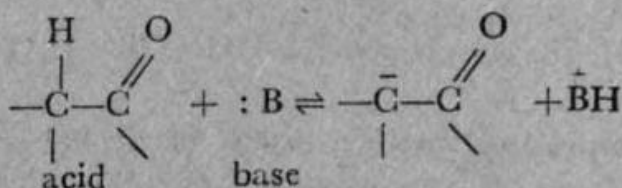
(6) **Reduction to Alcohols:** (a) Aldehydes on hydrogenation in the presence of a metal catalyst form primary alcohols, whereas under similar conditions ketones form secondary alcohols.



(7) **Aldol Condensation:** The carbonyl carbon atom which bears a partial positive charge due to the polarization of the carbon—oxygen double bond, exerts more attraction on the σ electrons between it and the α -carbon. The α -carbon, therefore, also bears a smaller partial positive charge and in turn attracts the σ electrons of a C—H bond to itself. Thus the α -hydrogen atoms are made slightly electrophilic or acidic in nature. The electron-withdrawing effect of the carbonyl group is shown below with the help of arrows :

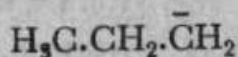


It is partly due to this reason that aldehydes and ketones having α -hydrogen atoms will react with bases to lose a proton to the base and themselves change to negatively charged ionic species.



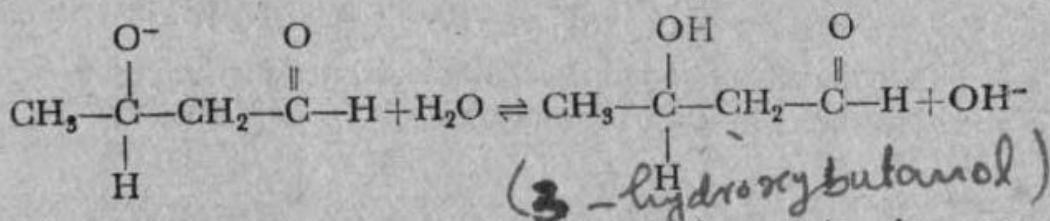
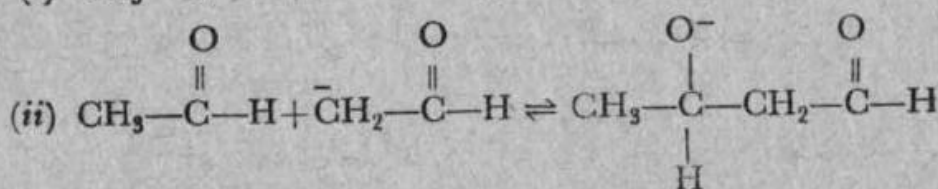
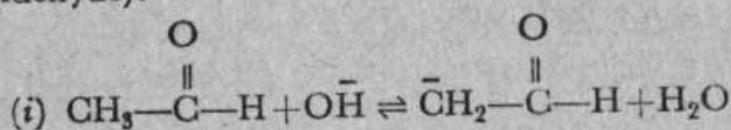
Another factor which makes the removal of α -hydrogen by base possible is that the charge density on the negatively charged carbon atom is reduced by the electron-withdrawing effect of the

carbonyl group. Thus an ion of this type is more stable than an ion of the type.



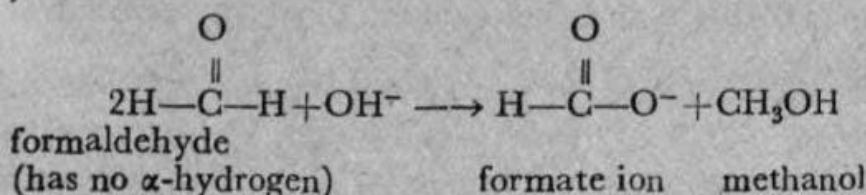
where a full unit charge is concentrated only on one atom.

Because of the acidity of the α -hydrogen atoms and because the resulting anion is stabilized by the adjacent carbonyl group, aldehydes and ketones having α -hydrogens react with bases according to the following sequence of reactions (illustrated by the reaction of acetaldehyde).



In the first reversible step, a carbanion is formed (an ion containing a negatively charged carbon atom which is bonded to three other atoms or groups of atoms is called *carbanion*). The carbon ion, which is nucleophilic, attacks the electrophilic carbonyl carbon atom of the unchanged acetaldehyde to form a new carbon-carbon bond (second step above). The resulting ion then accepts a proton from the solvent water giving aldol and at the same time regenerating the basic catalyst, OH^- . *Aldols* are so called because they are aldehydes as well as alcohols. All aldehydes and ketones which have α -hydrogen atoms undergo aldol condensation.

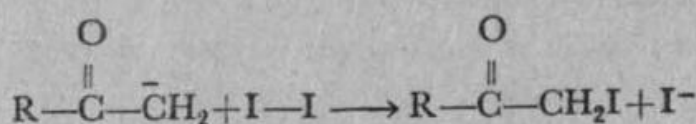
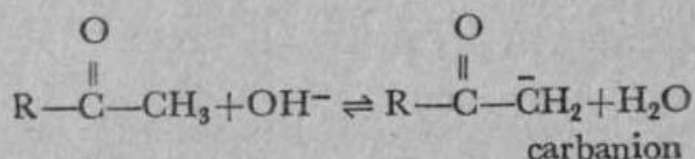
(b) **Cannizzaro Reaction:** Aldehydes which do not have any hydrogen atom on the α -carbon atom do not undergo aldol condensation. Instead they react with a concentrated solution of a base (NaOH or KOH) in water as follows :



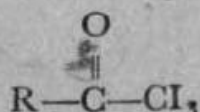
It is seen that one half of the aldehyde is reduced to the corresponding alcohol, while the other half is oxidized to an acid by a self-oxidation—reduction process. The reaction is called the *Cannizzaro* reaction. Reactions of this type, which involve self-oxidation-reduction processes, are called *disproportionation* reactions.

(c) **The Haloform Reaction :** Acetaldehyde and methyl ketones react with a solution of iodine in aqueous sodium hydroxide to form iodoform (CHI_3 , tri-iodo methane).

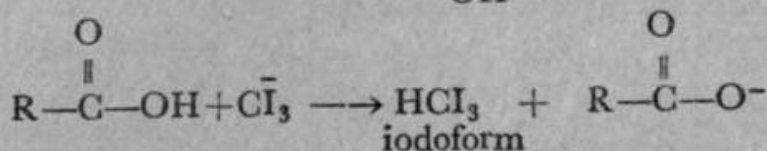
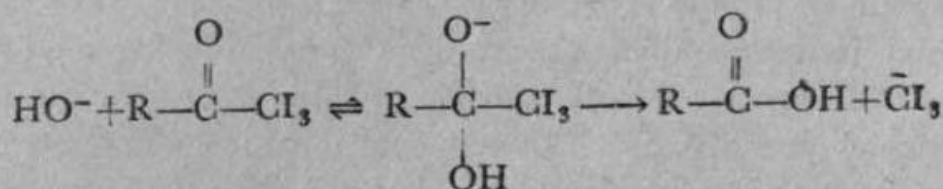
Like the aldol condensation, this reaction is also initiated by the attack of the base on an α -hydrogen.



The moniodocompound is readily iodinated further by a repetition of the above steps into a tri-iodocompound,

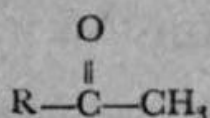


which then reacts further as follows :



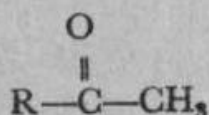
Iodoform (CHI_3) is a yellow solid and precipitates out from the reaction mixture.

A similar reaction will occur with bromine in aqueous sodium hydroxide with chlorine and aqueous sodium hydroxide to yield bromoform (CHBr_3) and chloroform (CHCl_3) respectively. Thus the reaction of

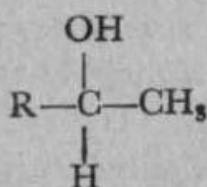


type compounds with a halogen in aqueous base called the *Haloform reaction*.

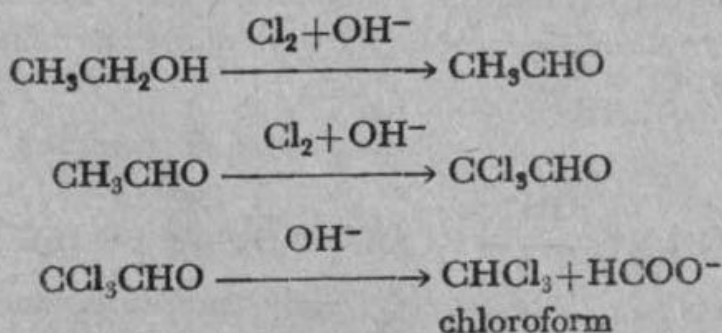
This reaction is not only given by $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$ type compounds but also by those compounds which can be easily oxidized to



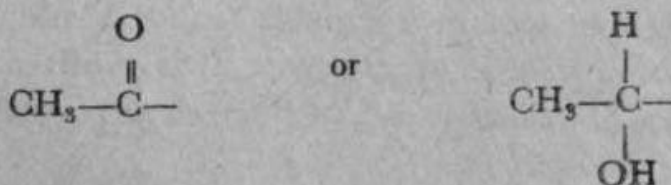
by the oxidizing action of the halogen in the presence of a base. Thus ethanol ($\text{CH}_3-\text{CH}_2\text{OH}$), and all secondary alcohols of the type,



also undergo the Haloform reaction *e.g.*,



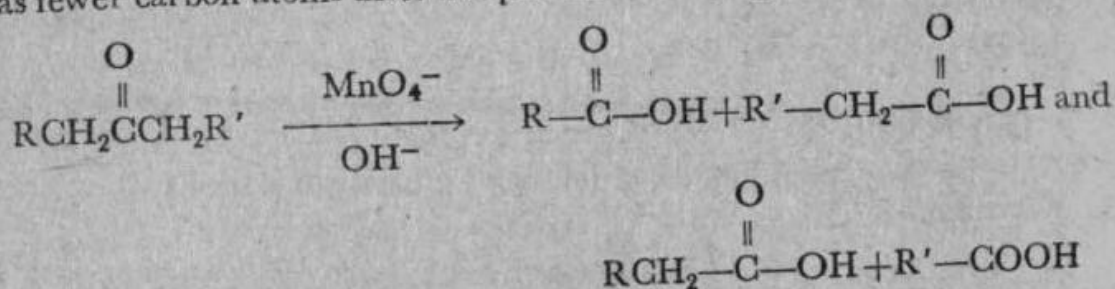
Since iodoform is a coloured solid, its formation from a compound when treated with $\text{I}_2 + \text{NaOH}$, is used as a quick test for the detection of



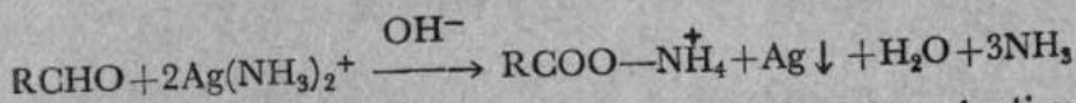
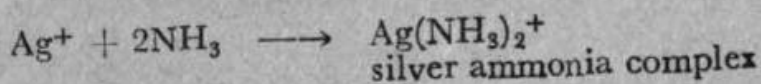
groups in an unknown compound. It is called the *iodoform test*. Chloroform and bromoform are colourless.

(8) Oxidation of Aldehydes and Ketones: Ketones are relatively resistant to oxidation. However, when strong oxidizing agents (*e.g.*, alkaline KMnO_4) are used, the carbon-carbon chain is

broken and a mixture of acids is formed. Each acid in the product has fewer carbon atoms than the parent ketone, *e.g.*,

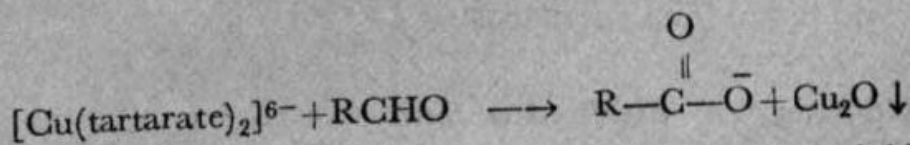
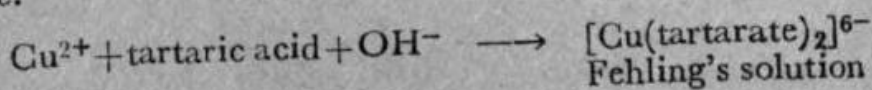


Aldehydes have a hydrogen atom directly bonded to the carbonyl group. They are, therefore, oxidized even by mild oxidizing agents into the corresponding carboxylic acids. The oxidation of aldehydes as compared to ketones is the basis of several tests for distinguishing aldehydes from ketones. One of these tests, the *Silver Mirror test*, uses silver ion as the oxidizing agent. The carbonyl compound is treated with an ammoniacal solution of silver nitrate (called *Tollen's reagent*). If the compound is an aldehyde it is readily oxidized to an acid by the silver ion, which is itself reduced to metallic silver. The metallic silver is deposited in the form of mirror on the walls of the test tube.



Tollen's reagent should be freshly prepared and discarded immediately after use. On standing it changes to highly explosive compounds.

In another test cupric ion is used as the oxidizing agent. The carbonyl compound is treated with an aqueous solution of a cupric salt, tartaric acid and sodium hydroxide (called *Fehling's solutions*). If the carbonyl compound is an aldehyde, it is oxidized to an acid and the cupric ion is reduced to a red brown precipitate of cuprous oxide.



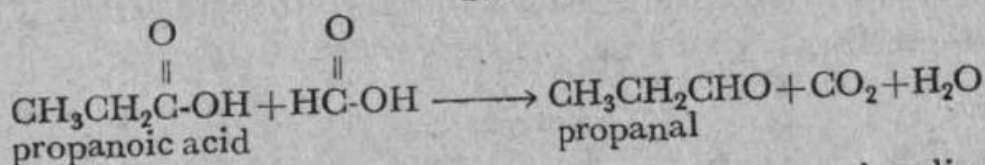
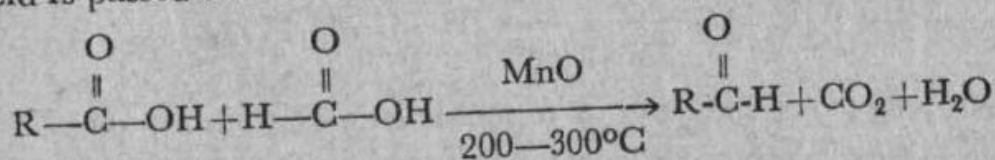
Note that the complex cupric tartarate ion is soluble in basic solution. Without tartaric acid, Cu^{++} precipitates out as $\text{Cu}(\text{OH})_2$.

If citric acid is used for complexing the cupric ion, the test solution is called *Benedict's solution*.

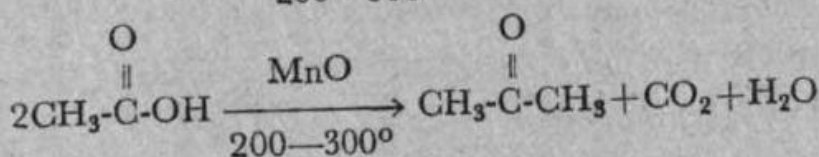
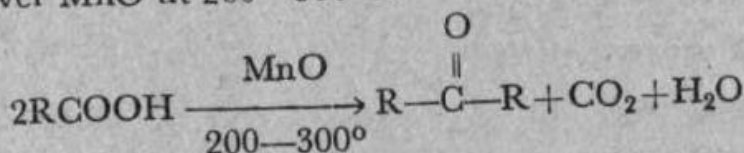
PREPARATION

(1) **Oxidation of Alcohols** : Formation of aldehydes and ketones by oxidation of the corresponding alcohols has been discussed in the chapter on alcohols.

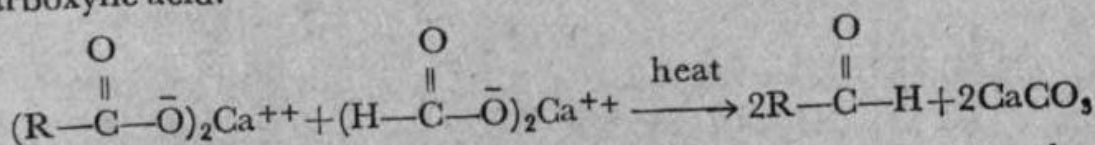
(2) **From Carboxylic Acids** : (a) Aldehydes are formed if a mixture of the vapours of formic acid and any other volatile carboxylic acid is passed over MnO at 200—300°C.



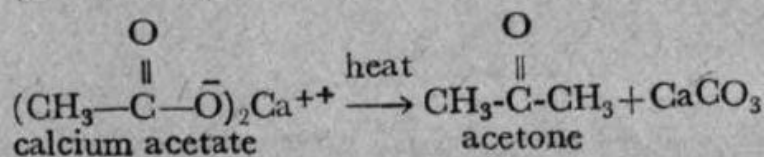
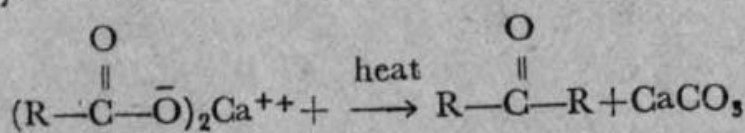
(b) Ketones are obtained if the vapours of a carboxylic acid are passed over MnO at 200—300°C.



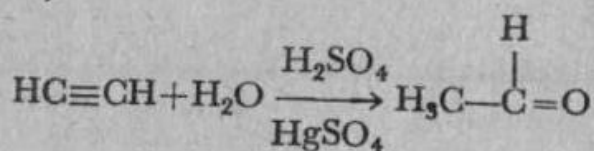
(c) Aldehydes are also obtained by the dry distillation of a mixture of calcium formate and the calcium salt of any other carboxylic acid.



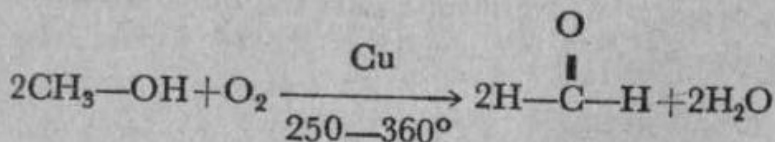
(d) Ketones are prepared by the dry distillation of the Ca salt of a carboxylic acid.



Acetaldehyde is commercially prepared by the hydration of acetylene in the presence of sulphuric acid and mercuric sulphate (see Chapter on hydrocarbons).



Formaldehyde is commercially prepared by passing a mixture of methanol vapour and air over a copper catalyst at 250–360°C.



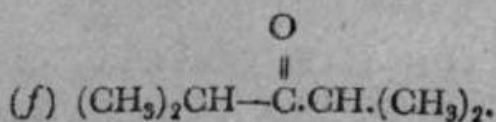
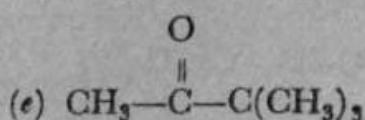
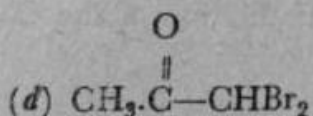
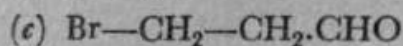
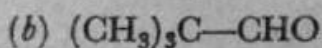
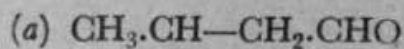
A 40% aqueous solution of formaldehyde containing about 8% methanol is used under the name, *Formalin*, for preservation of biological specimens.

Questions

1. Write the structural formulas of the following :

- 2-methyl-propanal;
- tri-chloroacetaldehyde;
- 2-bromo propanal;
- 1-bromopropanone;
- 3-methyl-2-butanone;
- 2-chloro-3-pentanone.

2. Name the following compounds :

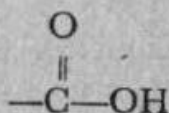


3. How does methanal differ from ethanal? Would you expect $(\text{CH}_3)_3\text{C}.\text{CHO}$ to resemble methanal or ethanal in chemical properties?
 4. The reaction between an aldehyde and NaCN takes place in the presence of small amounts of mineral acid. What would happen if a large amount of the acid were employed?
 5. What product (s) would be formed by distilling?
 - (a) calcium formate;
 - (b) a mixture of calcium acetate and calcium propionate.
 6. Hydration of ethyne gives ethanal. What product would you expect from the hydration of propyne? Give reasons.
 7. You are provided with a mixture of propanone and 3-pentanone. How would you bring about their chemical separation?
 8. How would you distinguish between?
 - (a) methanal and ethanal;
 - (b) ethanal and propanone; and
 - (c) butanone and butanal.
 9. 1-propanol and 2-propanol are isomeric and are readily oxidized to an aldehyde and a ketone respectively. Could you employ these oxidation products for confirming the structure of the two alcohols?
 10. Write down the structures of an aldehyde and a ketone having the molecular formula $\text{C}_4\text{H}_8\text{O}$. What chemical reaction would you perform in order to assign the identity of the two?
 11. Using ethyne as a starting material how would you get acetaldehyde, acetone and ethyl alcohol?
 12. Write equations for the following reactions :
 - (a) aldol condensation of propanal;
 - (b) Cannizzaro's reaction with benzaldehyde;
 - (c) methyl magnesium iodide with 2-butanone.
-

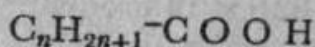
CHAPTER 17

CARBOXYLIC ACIDS

Organic compounds which contain the functional group,

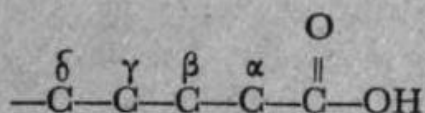


in their molecule are called *carboxylic acids*. Aliphatic carboxylic acids have the carboxyl group attached with an open chain of carbon atoms. They may be represented by the general formula

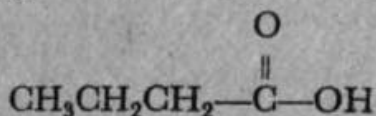


$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{OH} \end{array}$ or $\text{R}-\text{C}-\text{OH}$, where $\text{R}=\text{H}$, or any alkyl group. There are organic compounds which contain more than one carboxylic groups in their molecule. Thus we have dicarboxylic acids, and tricarboxylic acids, etc.

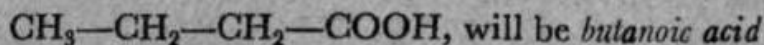
Nomenclature : (1) Many carboxylic acids are known by their common names, which were given to them before the systematic names were evolved. The positions of other groups attached with the chain containing the carboxyl group are indicated by the Greek letters α , β , γ , δ etc. The carbon adjacent to the carboxylic group is called the α (alpha) carbon ; the carbon atom in the carboxyl group is *not* the α carbon, *e.g.*



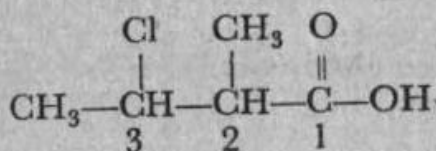
(2) The IUPAC system. From the name of the alkane, which contains the same number of carbon atoms as the longest continuous chain containing the carboxyl group, the ending-*e* is dropped and in its place the ending *-oic acid* added. For example, the carboxylic acid



has four carbon atoms in the chain containing the carboxyl group. The name of the alkane having a straight chain of four carbon atoms is butane. Therefore the name of the four carbon acid,

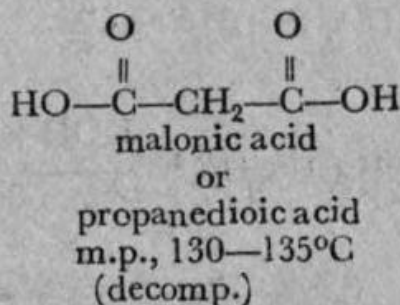
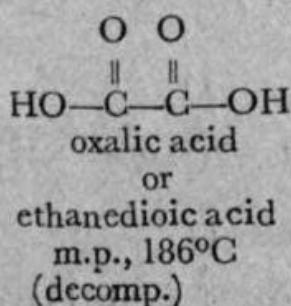
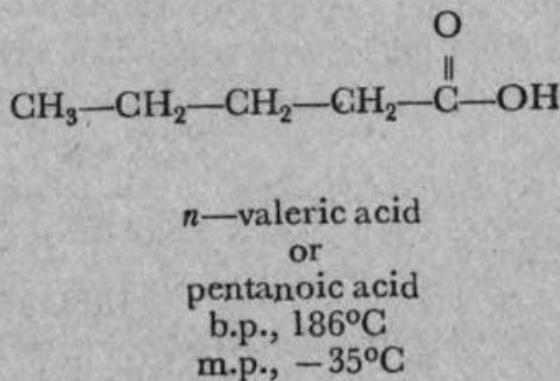
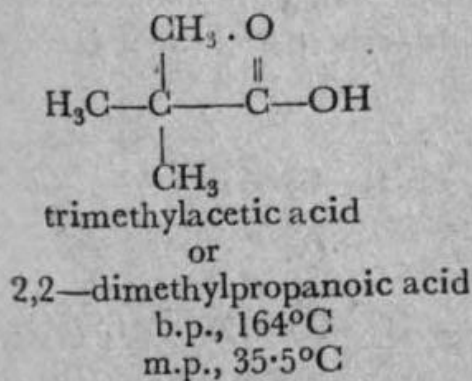
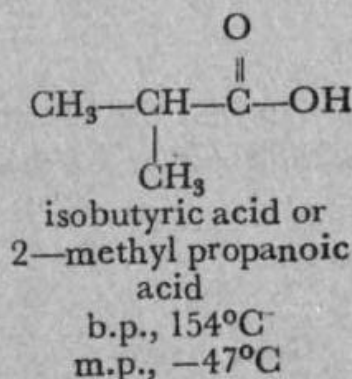
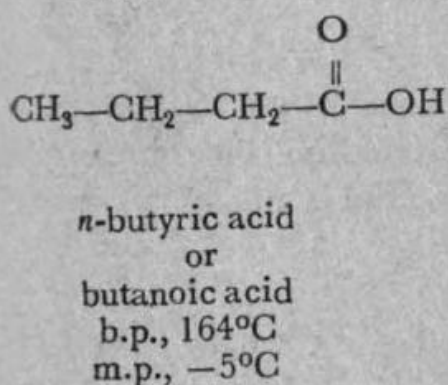
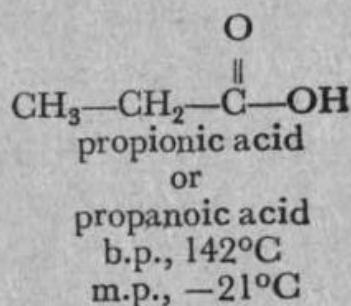
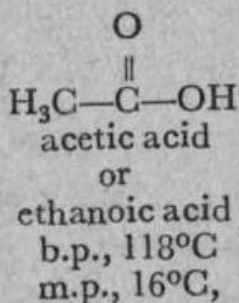
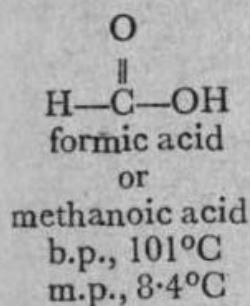


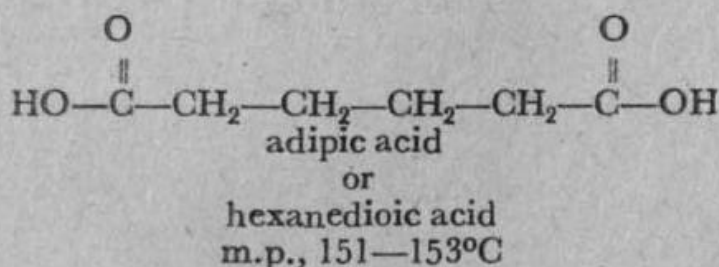
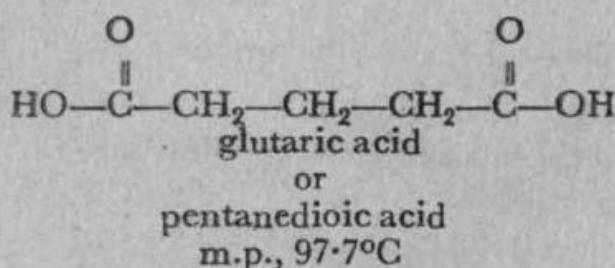
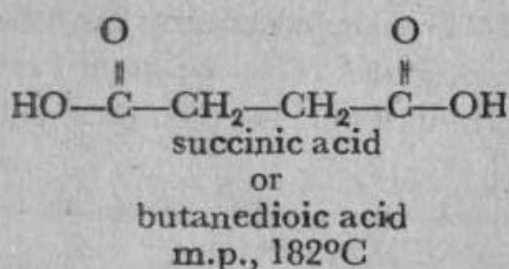
The carbon atoms of the chain containing the carboxyl group are numbered to indicate the positions of other groups attached with it. The carbon atom of the carboxyl group is given the number 1, *e.g.*,



3-chloro—2—methylbutanoic acid

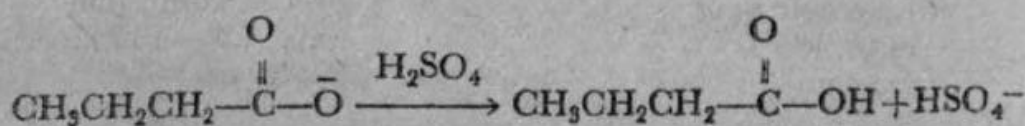
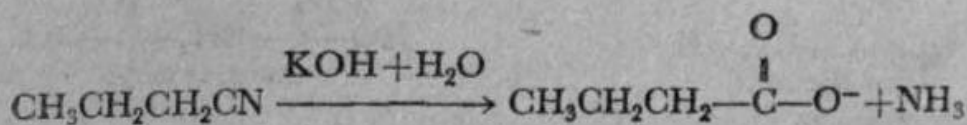
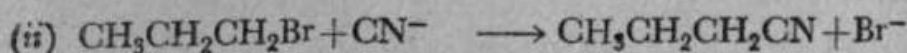
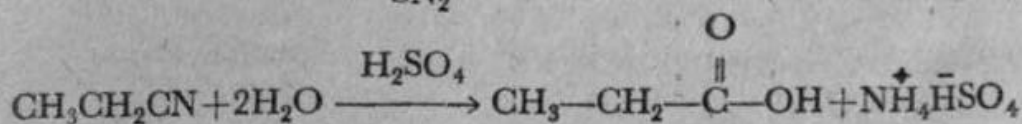
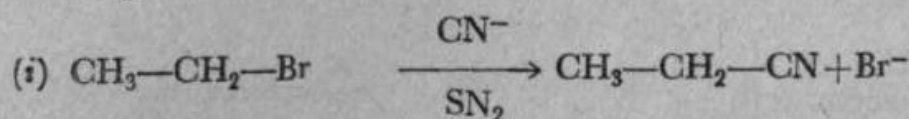
The names, and the structural formulas of a few carboxyl acids are given below. Boiling points and melting points are also given.



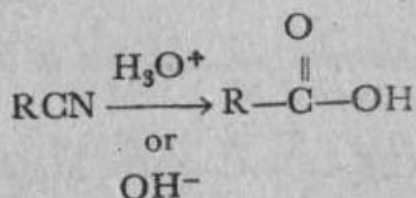
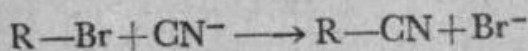


Note that the dicarboxylic acids are named in the IUPAC system by adding *dioic acid* to the name of the alkane containing the same number of carbon atoms as the carbon chain containing the two carboxyl groups.

Preparation : (1) Hydrolysis of Nitriles. A common method of preparation is the hydrolysis of a *nitrile*, which is in turn obtained from an alkyl halide (see Chapter 14). The hydrolysis of a nitrile is carried out with aqueous acid or with an alkali.

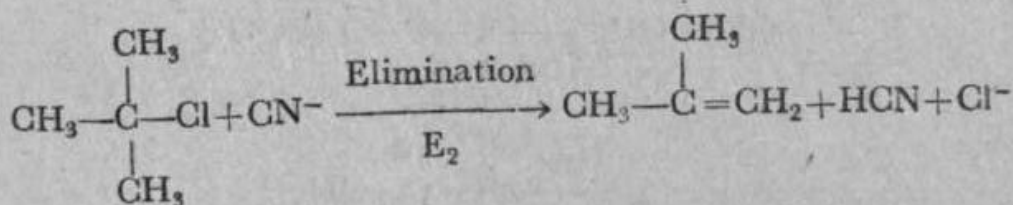


A general equation for the preparation of acids by this method is



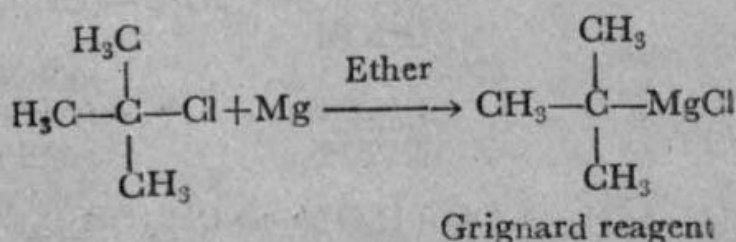
This method is particularly important because the carboxylic acid obtained has *one* carbon atom more than the number of carbon atoms in the alkyl halide from which it is made.

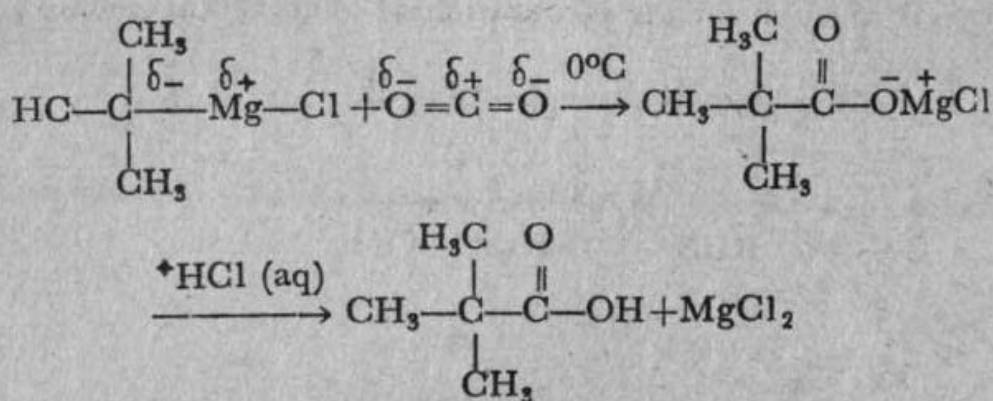
The method is useful only for the preparation of carboxylic acids from primary, and secondary alkyl halides. A tertiary alkyl halide when treated with cyanide ion (KCN or NaCN) undergoes elimination, to give an alkene rather than substitution to give a nitrile.



The yield of carboxylic acid is high from a primary alkyl halide, low from a secondary alkyl halide and negligible from a tertiary alkyl halide. Even with a secondary alkyl halide substitution of halogen by the nitrile group is accompanied by dehydrohalogenation (elimination).

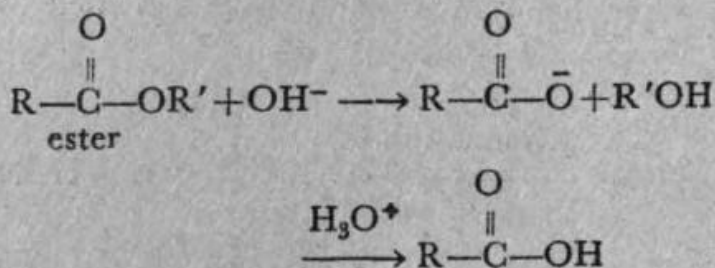
(2) **From Grignard Reagents :** The reaction of carbon dioxide with Grignard reagents followed by treatment with an aqueous acid yields carboxylic acids (Chapter 14). This method is used especially for making carboxylic acids from tertiary alkyl halides.



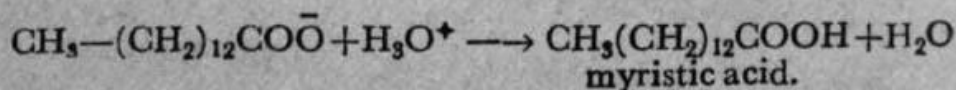
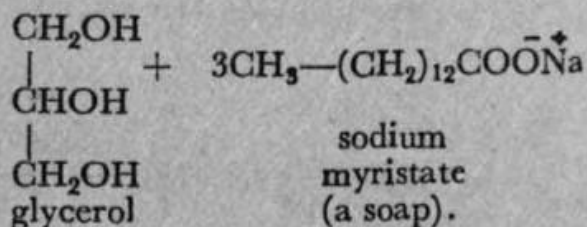
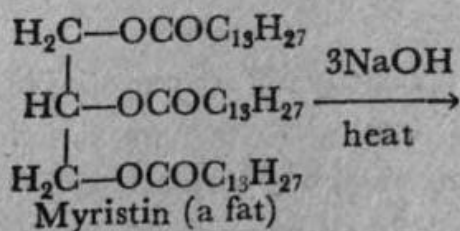


In this method also the carboxylic acid has one carbon atom more than the starting alkyl halide.

(3) **Hydrolysis of Esters :** Esters of carboxylic acids $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{R}'$ on hydrolysis with aqueous base yield alcohol and acid (Chapter 15).

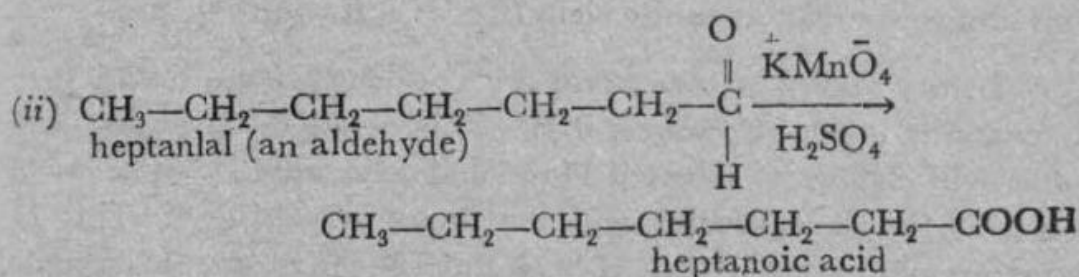
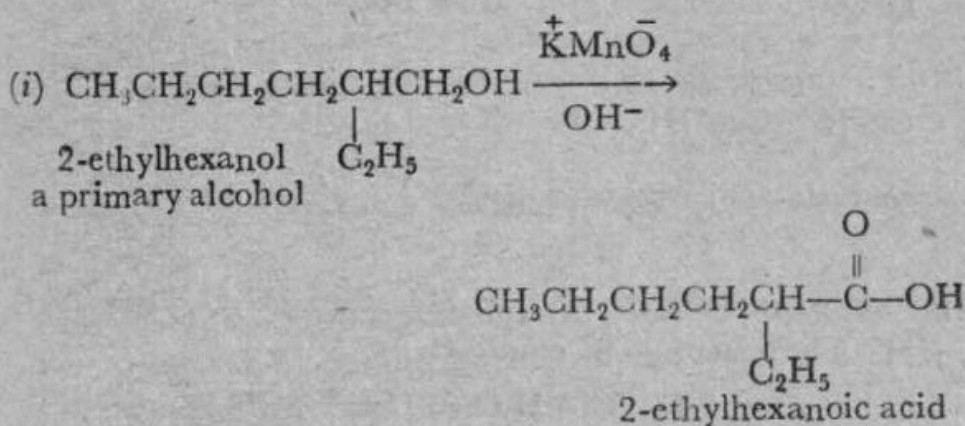


In the chapter on alcohols it was shown how glycerides (fats and oils) on treatment with aqueous base yield glycerol and the sodium salts of higher fatty acids (soaps.) A free carboxylic acid can be generated from the soap by treatment with an inorganic acid. Another example is given here.

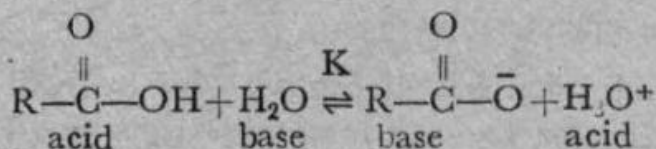


Aliphatic carboxylic acids are also called fatty acids because their higher homologues are constituents of fats and oils. Thus long chain carboxylic acids are called higher fatty acids.

(4) **Oxidation of Aldehydes and Alcohols :** Aldehydes and primary alcohols are oxidized to carboxylic acids when treated with potassium permanganate, nitric acid, or potassium dichromate in sulphuric acid.



Reaction : (1) Dissociation of Carboxylic Acids. When a carboxylic acid is dissolved in water the following equilibrium is established:



The extent to which the carboxylic acid ionizes in aqueous solution is given by the following equilibrium expression.

$$\begin{array}{c}
 \text{O} \\
 || \\
 \text{K} = \frac{[\text{R}-\text{C}-\text{O}^-] [\text{H}_3\text{O}^+]}{[\text{R}-\text{COOH}] [\text{H}_2\text{O}]} \\
 \text{or} \\
 \text{K}_a = \frac{[\text{RCOO}^-] [\text{H}_3\text{O}^+]}{[\text{RCOOH}]}
 \end{array}$$

where $\text{K}_a = \text{K} \cdot [\text{H}_2\text{O}]$. Thus the concentration of water, which is large and therefore remains essentially constant is included in the constant, K_a .

K_a is known as the *ionization constant* or the acid *dissociation* constant. The value of K_a for carboxylic acids is approximately 10^{-5} , i.e.,

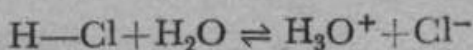
$$K_a = 10^{-5}$$

The ionization constants of acetic acid and α -chloroacetic acid may be compared.



Chloroacetic acid which has larger K_a is the stronger acid of the two.

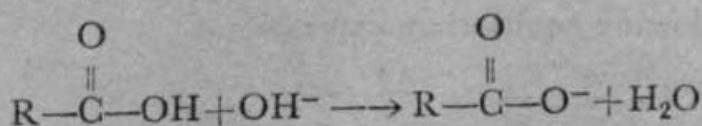
Mineral acids such as HCl , H_2SO_4 , and HNO_3 are almost completely ionized in water. The equilibrium



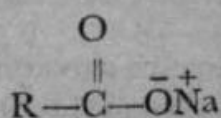
lies almost completely to the right (for HCl , $K_a = 10^{+8}$)

In dry $\text{HCl}_{(\text{gas})}$, two atoms are covalently bonded and the bond is partially ionic. However, if $\text{H}-\text{Cl}$ is dissolved in water almost all of it will change to solvated H_3O^+ and solvated Cl^- . The covalently bonded $\text{H}-\text{Cl}$ molecules will be almost nonexistent. This is why aqueous solutions of $\text{H}-\text{Cl}$, H_2SO_4 , and $\text{H}-\text{ClO}_4$, etc., are symbolized as H_3O^+ . Carboxylic acids are said to be much weaker than the mineral acids, because only a small percentage of their molecules is changed to H_3O^+ and anion in aqueous solution.

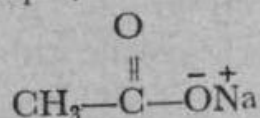
Carboxylic acids react instantaneously with hydroxide ion (OH^- , from NaOH , KOH , etc., is a much stronger base than H_2O) to form the carboxylate ion and water.



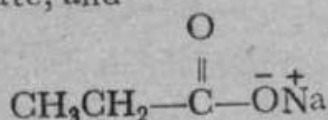
If an aqueous solution of NaOH is added to a carboxylic acid, the above reaction takes place. The reaction solution will also contain the solvated sodium ion, Na^+ . If water is evaporated a solid will be obtained which will have the composition :



It is the sodium salt of the carboxylic acid and is called sodium carboxylate. For example,



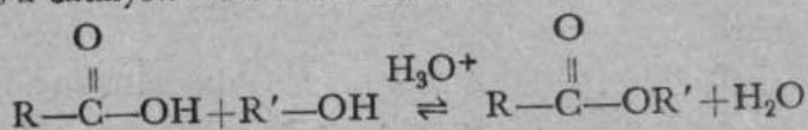
is called sodium acetate, and



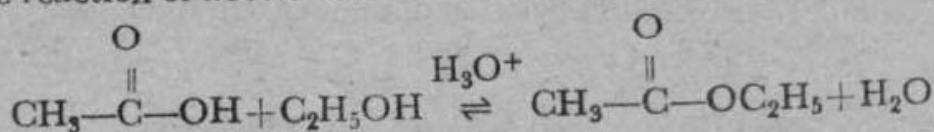
is called sodium propionate. In aqueous solution, however, the carboxylate ion is independent of Na^+ , and each one is surrounded

by water molecules. There is nothing like $\text{R}-\overset{\overset{\text{O}}{\parallel}}{\text{C}}-\text{O}-\text{Na}$ in aqueous solution.

(2) **Ester Formation :** Carboxylic acids react with alcohols to form *esters* and water in the presence of a small amount of $\text{H}-\text{Cl}$, or H_2SO_4 as a catalyst. The reaction is reversible :



For the reaction of acetic acid with ethanol

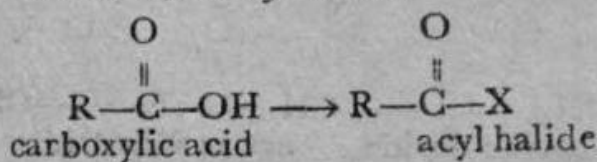


the equilibrium constant, K , has a value of about 4, i.e.,

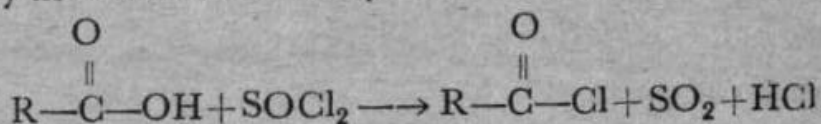
$$K = \frac{[\text{CH}_3-\overset{\overset{\text{O}}{\parallel}}{\text{C}}-\text{OC}_2\text{H}_5] [\text{H}_2\text{O}]}{[\text{C}_2\text{H}_5\text{OH}] [\text{CH}_3\text{COOH}]}$$

It means that the equilibrium is established when only about 66% of each reactant has been converted to ester. One way to drive the reaction to completion is to remove water from the reaction mixture as soon as it is formed (Le Chatelier Principle, Chapter on Chemical Equilibrium, Chemistry Part 1).

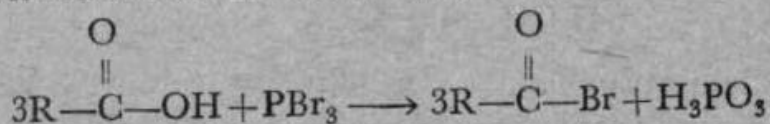
(3) **Formation of Acid Halides :** Like the $-\text{OH}$ group of alcohols, the OH part of a carboxyl group can be replaced by a halogen atom, giving what are known as *acyl halides*.



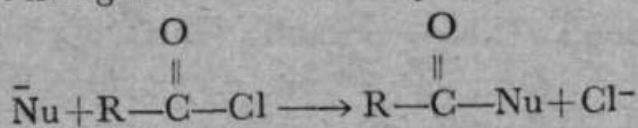
The $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-$ group is called the *acyl* group. Acyl-chlorides are mostly prepared by the reaction of thionyl chloride with a carboxylic acid.



Phosphorus halides are also used to make acyl halides.



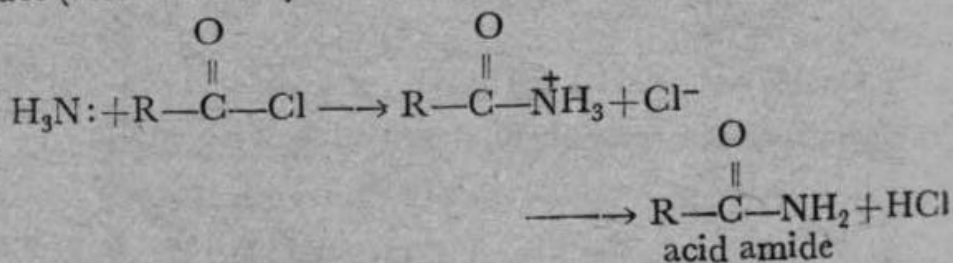
The acyl halides are of interest because the carbonyl carbon atom is electrophilic in nature and the halide ion is a good leaving group. Thus when a nucleophilic reagent will attack the electrophilic carbon atom, the halogen atom will be replaced readily.



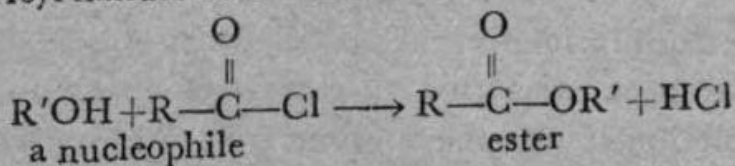
δ^+
a nucleophile

(a simplified view of the reaction of a nucleophile with an acyl halide)

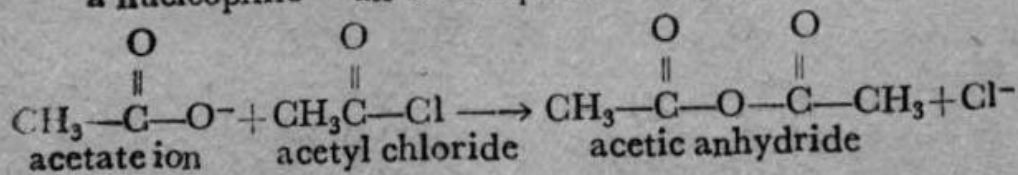
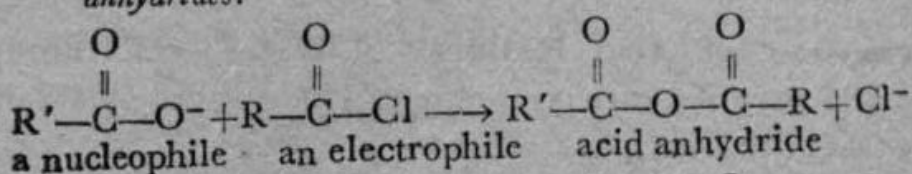
(i) Acyl chlorides react with ammonia (a nucleophile) to give amides (also recall acylation of amines, Chapter 14).



(ii) Acyl halides react with alcohols to form esters

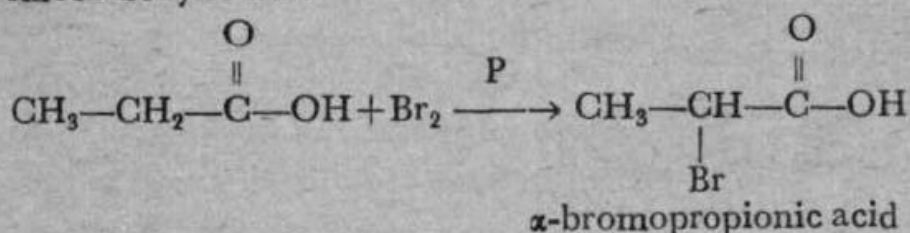


(iii) Acyl halides also react with carboxylate ions to form anhydrides.



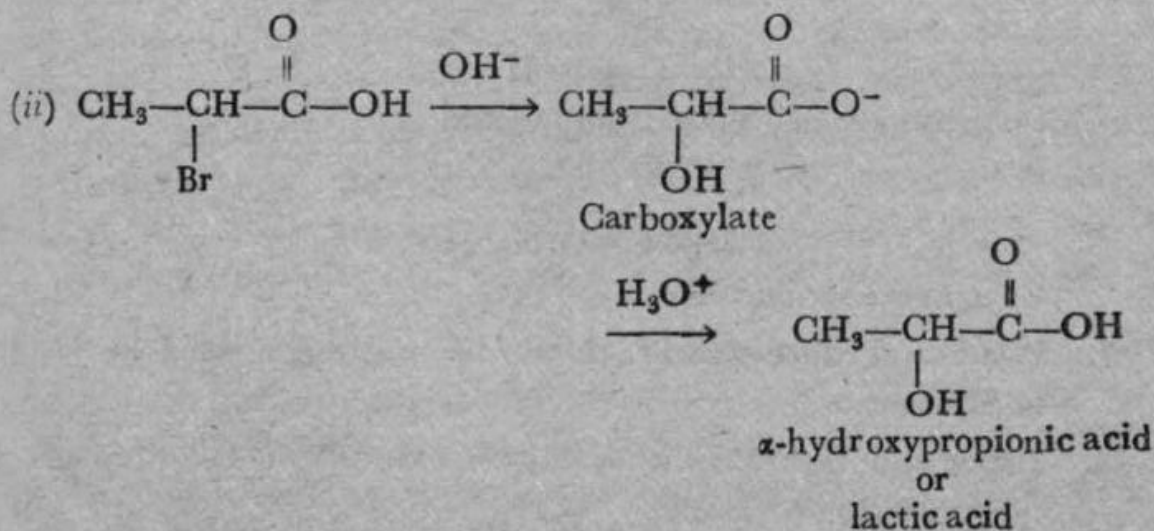
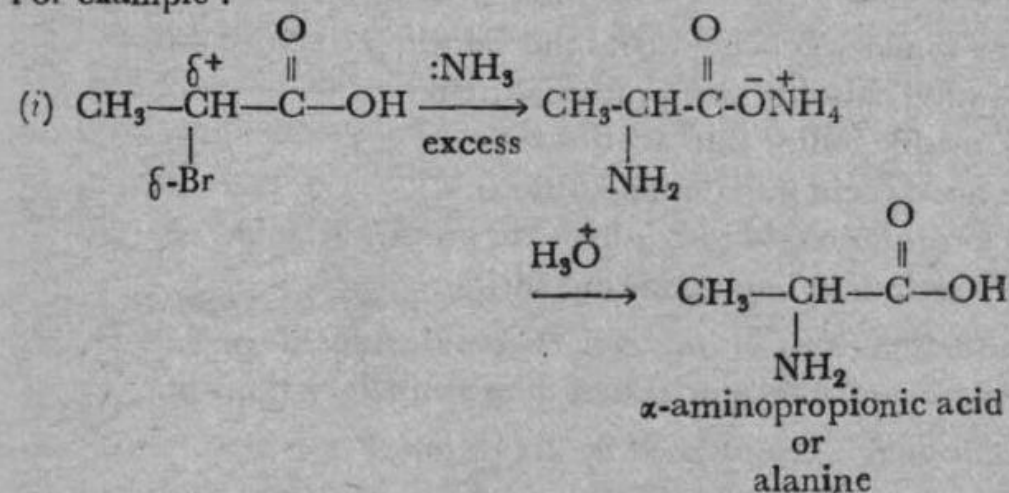
Anhydrides are so called because they may be regarded as having been formed by a combination of two molecules of acid by **elimination** of one molecule of water.

(4) Halogenation of the Alkyl Group : Carboxylic acids react with bromine in the presence of small quantities of phosphorus to form α -bromocarboxylic acids.



The α -carbon atom being bonded to a more electronegative atom bears a partial positive charge. A variety of nucleophiles can attack the electrophilic α -carbon displacing the halogen atom.

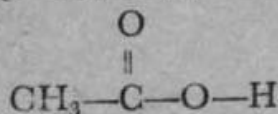
For example :



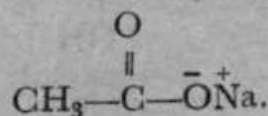
Note that NH_3 and OH^- first react with the carboxyl group to remove its proton forming the carboxylate ion of the α -haloacid, which then undergoes substitution of the halogen atom by the second molecule of the nucleophile. The free hydroxy acid or amino acid is then regenerated by adding a strong acid such as H_2SO_4 or HCl .

Questions

1. Write structural formulas of the following :
 - (a) 5-bromopentanoic acid,
 - (b) 2, 3-dimethyl butanoic acid,
 - (c) α -chlorosuccinic acid,
 - (d) propionamide,
 - (e) calcium acetate.
2. Name the following :
 - (a) $(\text{CH}_3)_2\text{CH}.\text{CH}_2\text{COOH}$
 - (b) $\text{HOOC}(\text{CH}_2)_3\text{COOH}$
 - (c) $\text{CH}_3\text{CH}_2\text{CO}.\text{Cl}$
 - (d) $\text{CH}_3.\text{CH}=\text{CH}.\text{COOH}$
 - (e) $\text{Cl}_3\text{C}.\text{COOH}$
3. Describe any two methods of lengthening a carbon chain.
4. How would you bring about the following conversions?
 - (a) ethyl chloride into propanoic acid,
 - (b) methyl iodide into acetic acid,
 - (c) acetic acid into amino acetic acid,
 - (d) propanoic acid into α -hydroxy propanoic acid,
 - (e) acetic acid into acetic anhydride.
5. The action of KCN on tertiary butyl chloride results in the formation of an alkene rather than a nitrile. Explain.
6. Acetic acid is represented by the structure.



whereas sodium acetate is formulated as



Explain the significance.

7. Would you expect acetic acid to be a stronger acid in H_2O or in benzene?
8. Define and illustrate with a suitable example the following :
 - (a) ionization constant,
 - (b) esterification,
 - (c) an acid amide,
 - (d) an acid anhydride,
 - (e) an acid chloride.

CHAPTER 18

AROMATIC HYDROCARBONS

In addition to the open-chain hydrocarbons described in Chapter 13 we have another class of hydrocarbons—the aromatic hydrocarbons. These are closed-chain or cyclic compounds. Benzene (C_6H_6), the simplest of these, is to aromatic hydrocarbons what methane is to the open-chain hydrocarbons.

The term *aromatic*, derived from the Greek word *aroma*, which means spice, arose from the fact that some of the compounds related to benzene, that were first isolated and examined, had pleasant spice-like odours. However, it must be kept in mind that this is no longer regarded as a characteristic property of aromatic compounds. At present, aromatic hydrocarbons are those that contain benzene nucleus in their molecules. In other words aromatic hydrocarbons are alkyl—rather aryl-derivatives of benzene.

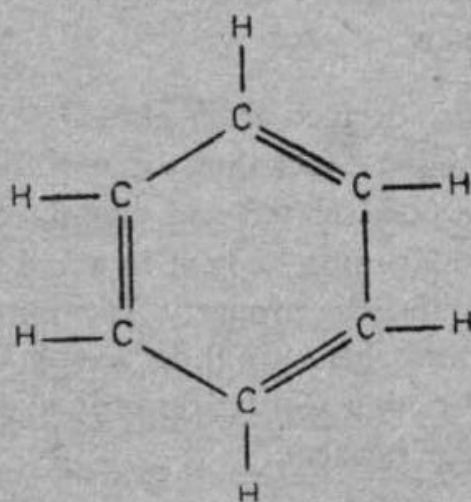
Structure of Benzene : It appears that benzene was first discovered by the English chemist Faraday in 1825. It melts at $5.5^\circ C$ and boils at $80^\circ C$. Its molecular weight was shown to be 78 and the molecular formula found to be C_6H_6 . Soon it was realised that the properties of benzene were such as to make it quite distinct from the other types of hydrocarbons known to chemists at that time. Benzene does not decolourize $KMnO_4$, nor does it decolourize bromine water. But then it does add six atoms of hydrogen and six atoms of bromine to form hexahydro benzene (C_6H_{12}) and benzene hexabromide ($C_6H_6Br_6$). Although first two reactions indicate absence of unsaturation in the molecule, the last two indicate the presence of the same.

Benzene behaves as if it were a saturated compound in that it forms substitution products on treatment with HNO_3 , H_2SO_4 and other reagents. All these reactions indicate that benzene is a new type of hydrocarbon which though unsaturated, nevertheless, behaves as if it were a saturated compound.

Structure of benzene, therefore, continued to intrigue the minds of chemists for a considerable time. The formula of benzene, obviously, does not correspond to any of the three types encountered in the earlier chapters. It is clearly seen that on the basis of an alkane, the formula

would have been C_6H_{14} , whereas on the basis of an alkene the formula would come C_6H_{12} . An alkyne structure is also ruled out as the formula would then be C_6H_{10} . We might, therefore, be tempted to say that benzene *does not belong to an open-chain hydrocarbon family*.

The solution of the benzene problem was given by the German chemist, Kekule (1865), who proposed a cyclic regular hexagonal structure for benzene (Fig. 18.1).



Kekule's Formulation of Benzene

Fig. 18.1

This structure of benzene is borne out by the following facts:

(1) When benzene is shaken with hydrogen and a nickel catalyst, in a pressure apparatus, hexahydrobenzene (C_6H_{12}) is formed. This is identical to cyclohexane obtained through a different route (Fig. 18.2).

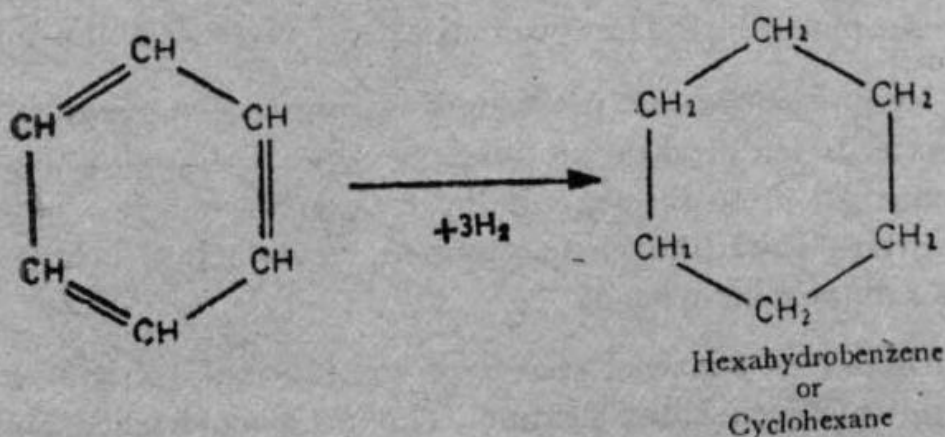


Fig. 18.2

Similarly, in the presence of sunlight, benzene adds six chlorine atoms forming benzene hexachloride (Fig. 18.3).

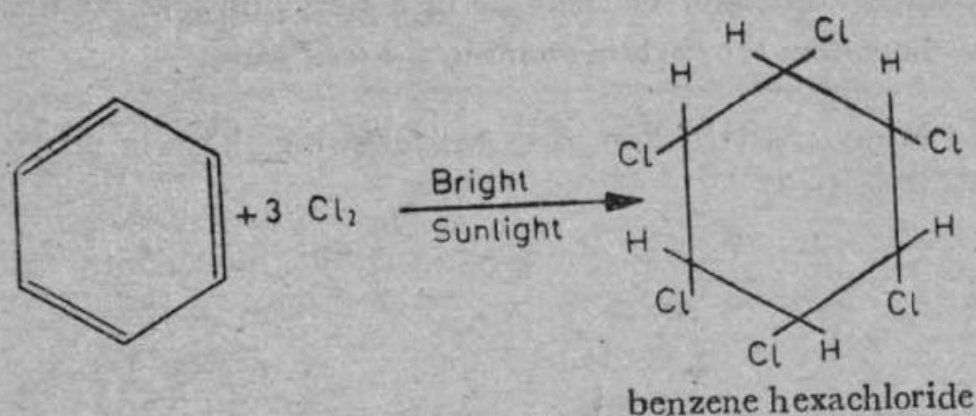


Fig. 18.3

These reactions indicate the presence of three double bonds in a molecule of benzene.

(2) There is only one mono-substitution product of benzene, having the general formula C_6H_5X , i.e., only one toluene $C_6H_5-CH_3$ or only one phenol C_6H_5OH exists. The existence of only *one* monosubstitution product of benzene follows logically from a regular hexagonal structure having double bonds alternating with a single bond.

(3) There are *three* isomeric disubstitution products of benzene, having the general formula $C_6H_4X_2$ or C_6H_4XY . Thus dimethyl benzenes (commonly called xylenes) exist in three isomeric forms distinguished by prefixes, *ortho*—, *meta*—, *para*— (Fig. 18.4).

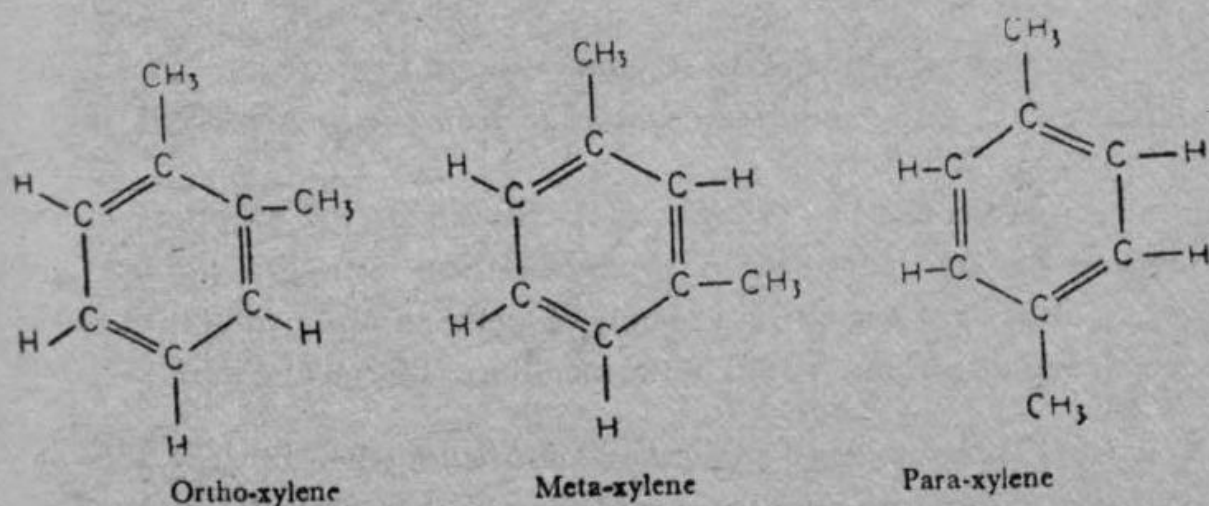


Fig. 18.4

It is thus seen that the existence of the three isomeric di-substituted benzenes follows from the structure proposed by Kekule.

(4) Convincing evidence for the Kekule structure of benzene has been furnished by X-ray analysis. This technique has shown that all the six carbon atoms of benzene lie in a *plane* and that the hydrogen atoms radiate from the carbon atoms in the *same plane*.

The X-ray analysis then gives the following shape to the benzene molecule (Fig. 18.5).

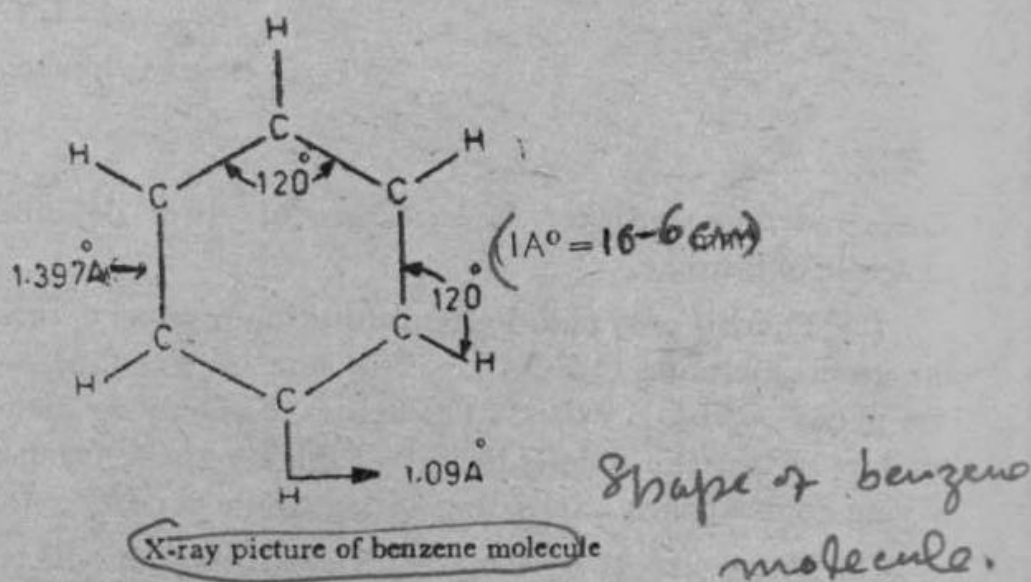


Fig. 18.5

Sources of Aromatic Hydrocarbons: Coal and Petroleum represent the major industrial sources of aromatic hydrocarbons.

(a) **From Coal:** When coal is heated in the *absence of air*, it decomposes into three main products—Coke oven gas, coal tar, and coke. Coke oven gas consists mainly of methane and hydrogen. Coke, which is pure carbon, is used in the metallurgy of iron and steel.

Coal tar is subjected to *fractional distillation* when benzene, toluene, xylenes, phenols, naphthalenes and many other aromatic compounds are obtained. In fact, over 215 aromatic compounds have been isolated from coal tar. The Table (18.1) below gives the percentage amount of the most important aromatic compounds obtained from fractional distillation of coal tar :

Table 18.1

CHIEF COMPONENTS OF COAL-TAR*

Compounds	Percentage
benzene	0.1
toluene	0.2
xylene	1.0
Naphthalenes	11.0
dimethyl naphthalenes	3.4
acenaphthene	1.4
fluorene	1.6
phenanthrene	4.0
anthracene	1.1
carbazole	1.1
phenols	2.5
pyridines	2.0

It has been calculated that 100 kgm. of coal tar gives 1.2 kgm. of benzene and its homologues.

(b) **From Petroleum** : Benzene and other aromatic hydrocarbons may be manufactured from petroleum by special cracking methods known as "hydro-forming". For example, *n*-hexane when passed over a platinum catalyst at 500°C, under a pressure of 45-225 kgm. forms benzene and hydrogen. The reaction is believed to proceed through the formation of cyclohexane (Fig. 18.6).

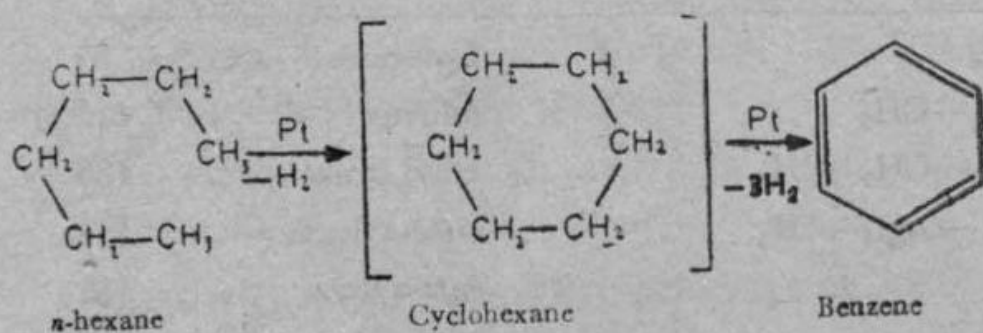


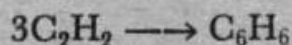
Fig. 18.6

n-heptane (C_7H_{16}), similarly, gives toluene ($\text{C}_6\text{H}_5-\text{CH}_3$).

*A ton of coal gives about 1,500 lbs. of coke, 100 lbs. of coal tar 1000—1,200 cubic feet coke oven gas, and 8.9 tons of water. The water thus obtained contains ammonia, from which about 20 lbs. of ammonium sulphate (used as a fertilizer) may be obtained.

An alternate procedure is to pass the vapours of *n*-heptane over a catalyst, consisting of $\text{Cr}_2\text{O}_3 + \text{Al}_2\text{O}_3$ and SiO_2 , at 500°C .

(c) **From Acetylene :** Acetylene, when passed over a large layer of finely divided nickel at a temperature of 150°C , is converted to benzene.



However, this process is of academic interest only and serves to demonstrate the relationship between open chain and closed chain hydrocarbons.

Homologues of Benzene : Benzene is the first member of aromatic hydrocarbons and its homologues are obtained by substituting one or more hydrogen atoms with methyl groups. (This process retains the ring character of the compounds). The following is a list of the more common homologues (Table 18.2).

Table 18.2

HOMOLOGUES OF BENZENE

Molecular formula	Common name	b.p. $^\circ\text{C}$	m.p. $^\circ\text{C}$.
C_6H_6	.. benzene	.. 80	5.5
$\text{C}_6\text{H}_5\text{—CH}_3$	.. toluene	.. 111	—95
$\text{C}_6\text{H}_5\text{—CH}_2\text{—CH}_3$	.. ethyl benzene	.. 136	—95
$\text{CH}_3\text{—C}_6\text{H}_4\text{—CH}_3$	.. <i>ortho</i> -xylene	.. 144	—25
	<i>meta</i> -xylene	.. 139	—48
	<i>para</i> -xylene	.. 138	—13.3

Nomenclature : The homologues of benzene, as is obvious from the above table, arise by substituting one or more hydrogen atoms of the ring by an alkyl group or groups. Hence the next member of the benzene family would be methyl benzene or *toluene*. Further addition of a $\text{—CH}_2\text{—}$ group would give rise either to ethyl benzene if substitution occurs at the methyl carbon, or to xylenes in case substitution occurs

at a ring carbon. The substitution at ring carbon may occur at either of the three points (Fig. 18.7).

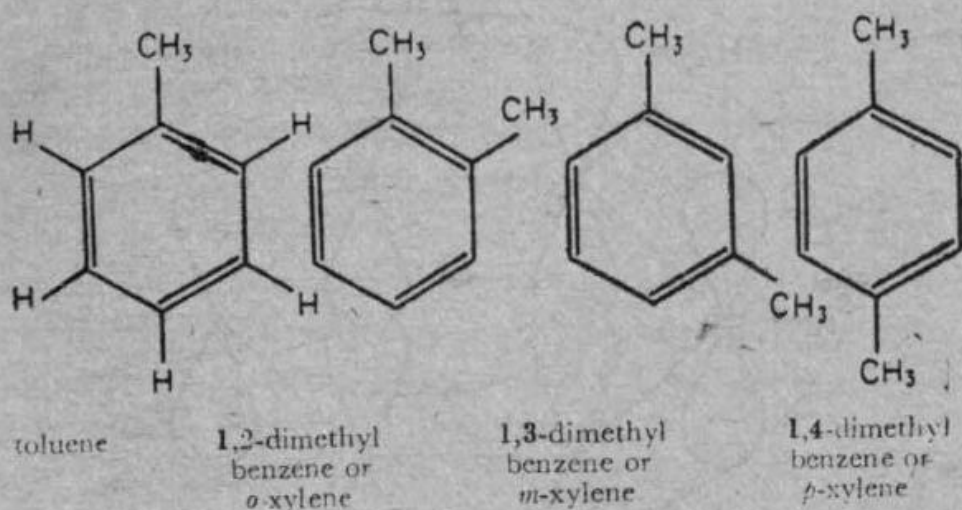
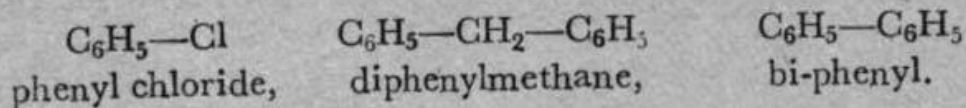


Fig. 18.7

It is clear from the formulas that 1,2—dimethyl benzene has two methyl groups on two adjacent ring carbons, 1, 3— isomer has the methyl groups on two carbon atoms separated by *one* carbon atom. The third, isomer, 1, 4—dimethyl benzene has the two methyl groups on carbon atoms directly *opposite* to one another. 1, 2—disubstituted benzenes are usually prefixed by *ortho*-or more simply by *o*—, the 1, 3—disubstituted ones are prefixed by *meta*-or *m*—, whereas the 1, 4—disubstituted benzenes are prefixed by *para*-or by *p*—.

As in the case of saturated hydrocarbons removal of one hydrogen atom from methane generated the *methyl* radical, similarly, removal of a hydrogen atom from benzene gives us the phenyl radical ($\text{C}_6\text{H}_5\text{—}$). The system is illustrated by following examples :



MODERN CONCEPT OF THE STRUCTURE OF BENZENE

(a) **Atomic Orbital Treatment of Benzene :** Atomic orbital treatment of benzene affords a reasonably good picture of benzene molecule. Each ring carbon may be taken as sp^2 hybridized thereby forming three equivalent, co-planar sp^2 hybrid orbitals. The electrons in two of these orbitals of each carbon atom are utilized in forming σ bonds with the two electrons of the sp^2 orbitals of two adjacent carbon atoms. The third electrons of the sp^2 hybrid orbital of each carbon

forms a bond with the $1s$ electron of a hydrogen atom. This bonding, then, gives the following picture of a benzene molecule (Fig. 18.8).

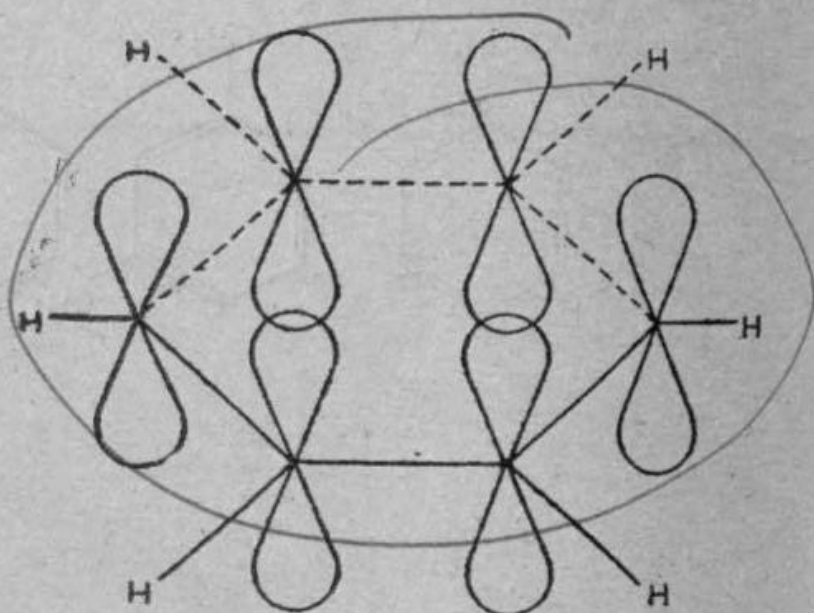


Fig. 18.8

As a result of this shape, the bond-angles between any three carbon atoms would be 120° and the carbon-carbon bond distance would be *uniform*. And as we have seen, earlier, these predictions have been borne out by X-ray analysis of benzene molecule.

The σ bonds to carbons and hydrogen atoms utilize three of the four valence electrons of each carbon atom. There remain six electrons, one on each carbon in its unhybridized p -orbital. Hence we could formulate three π -bonds (by analogy with ethene) through sidewise overlap of adjacent p -orbitals. However, as a result of the regular hexagonal shape of the benzene ring, it would be obvious that the π -electrons are perfectly paired all the way right round the ring. See diagram (Fig. 18.9).

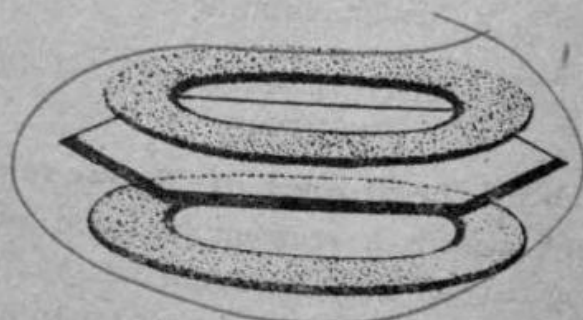


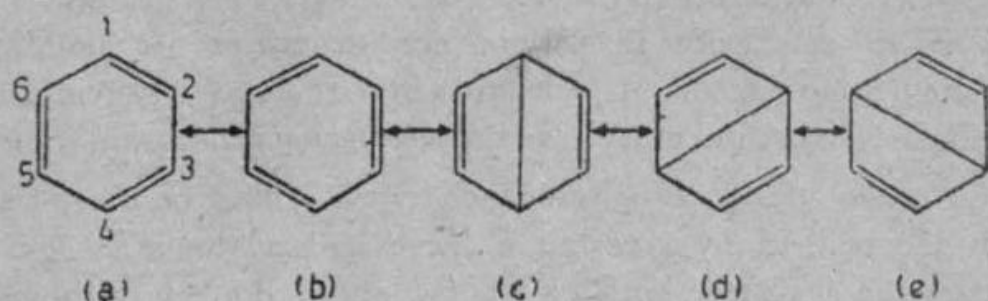
Fig. 18.9

By virtue of the above treatment we now have six π -bonds (rather than the conventional 3 bonds), all in *one continuous sheath*. These π -

electrons get associated with all the six carbon atoms in a region *above and below* the plane of the benzene ring.

A watchful student, at this stage, would differentiate between π -bonding as seen in alkenes and the one described above. In alkenes, we are primarily concerned with isolated double bonds, and hence any π -bonding that may be involved is entirely between the two carbon atoms joined by the double bond. In benzene we have, what we term as conjugated double bonds (double bonds alternating with single bonds), and as each carbon atom has a p -electron, the resulting π -overlap becomes *extensive* and completely buries the benzene ring within itself. We may say that π -electrons in benzene ring are much more *delocalized* than in a typical alkene. It is this extensive π -electron delocalization which is responsible for the special chemical behaviour of benzene.

(b) **The Resonance Method :** The atomic-orbital treatment of the benzene problem immediately suggests that there are many different ways of pairing of the fourth valence electron (the p -electrons) of each carbon atom. These different *pairing* schemes would lead to the following double bond structures for benzene (Fig. 18.10).



Different pairing schemes of six p -electrons of benzene

Fig. 18.10

Figures (a) and (b) are the two identical Kekule structures. They are similar to one another in all respects. The only difference is that in (a), the pairing has taken place between carbon number 1 and 2, 3 and 4, and 5 and 6, whereas in (b), the pairing has occurred between carbon numbers : 2 and 3, 4 and 5 and 6 and 1. The structures (c), (d), and (e), although still regular hexagons, nonetheless represent entirely different pairing arrangements in that the C_1-C_4 , C_2-C_5 , C_3-C_6 bonds are far too apart for effective bond formation. Hence these three structures would be energetically less favourable than the two identical Kekule structures—(a) and (b). Structures (c), (d), and (e) are called *Dewar* structures.

The structures (a) to (e) represent different pairing schemes of the fourth electron of each carbon atom in the benzene ring. Such structures are frequently called *resonance structures*. A resonance structure has *no tacit physical existence*; all it implies is that different pairing schemes of *p*-electrons are available. As a result of these different pairing arrangements actual energy of the benzene molecule is *less* than that expected on the basis of any of the structures given in Figure (18.10). However, contribution of structures (a) and (b) to the actual state of the benzene molecule would be much greater than that of structures (c) to (e).

The resonance treatment, then, implies that benzene can be represented by neither of the two Kekule structures nor by any of the structures shown in (c) to (e), but by a structure which has the *character of all the five structures*. Obviously the two Kekule structures contribute largely to what is termed as the *resonance hybrid*. Thus the actual mode of pairing of the fourth electron of each benzene ring carbons cannot be represented by one structure. The resonance hybrid—the actual molecule—cannot be picturised, but it possesses the character, principally, of the two Kekule forms and to a less extent of the three forms (c) to (e). Needless to emphasise that resonance structures are nothing but alternate pairing schemes of *p*-electrons in a conjugated system and that all resonance structures must have the *same spatial arrangement of atoms*.

(A crude analogy of a resonance hybrid would be that of a mule which is obtained by crossing a horse and a donkey. The mule possesses the character both of a horse and a donkey, although it is neither of them. However, a glaring difference between the horse-donkey hybrid and the benzene hybrid is that the horse and the donkey have real existence, but the Kekule and Dewar structures of which benzene is considered to be a hybrid, exist only in imagination).

Resonance structures are connected by a double headed arrow ($\longleftrightarrow$).

To simplify the treatment, we might say that benzene is a resonance hybrid, principally, of two Kekule forms as shown in Fig. 18.11.

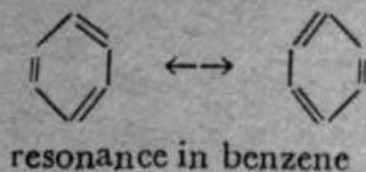


Fig. 18.11

Clearly it is inconvenient to always write down the structures of the contributing forms in order to show the nature of the hybrid. Hence it is a common practice to use a single Kekule structure, *i.e.*, Fig. 18·10 (a) or (b), to represent benzene with the implicit understanding that C—C bonds are all equivalent.

Both the atomic orbital treatment and the resonance treatment describe benzene as a symmetrical structure with a uniform C—C bond distance. At this stage it is of interest to keep in mind the C—C bond distances in the four types of hydrocarbons.

Table : BOND LENGTH IN C—C COMPOUNDS

C—C bond distance in alkanes	=	1·54 Å°
C—C bond distance in alkenes	=	1·34 Å°
C—C bond distance in alkynes	=	1·20 Å°
C—C bond distance in benzene	=	1·397 Å°

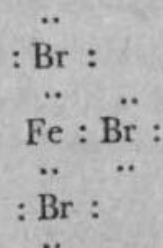
It is obvious that the value for benzene is the same for all the bonds in the hexagon and that it corresponds neither to a single covalent bond length nor to a double covalent bond length. The data obviously appears to have an intermediate value, which gives the benzene molecule its typical character; neither a truly double bonded molecule nor a truly single bonded molecule.

GENERAL PATTERN OF THE CHEMICAL REACTIVITY OF BENZENE

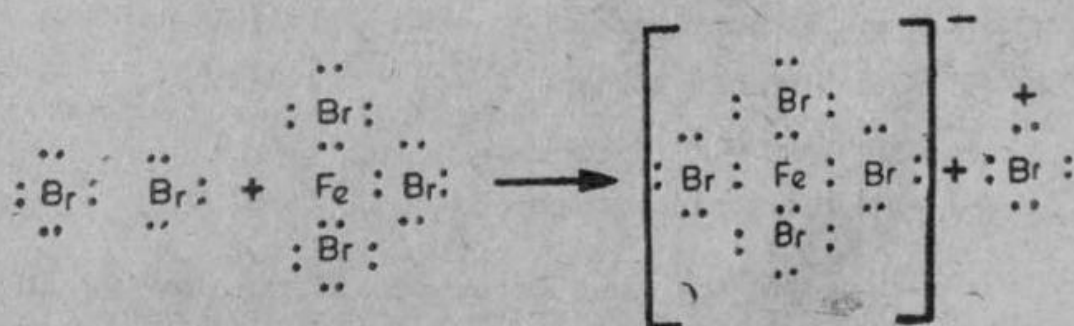
Benzene like an alkene possesses a π —electron system and as such would be expected to undergo electrophilic attack similar to that on alkenes. However, as the π —electron system of benzene is very markedly stabilized by resonance, the electrophilic attack on benzene compounds has certain features which *differ* from electrophilic attack on alkenes. The π —electrons of the benzene ring are not as readily available as in alkenes, and hence *do not assist* in the attack of a weak electrophile in the same way, the π —electrons of an alkene do.

Hence a more powerful electrophile is required for a successful attack on the π —electrons of benzene than is needed for attack on an alkene.

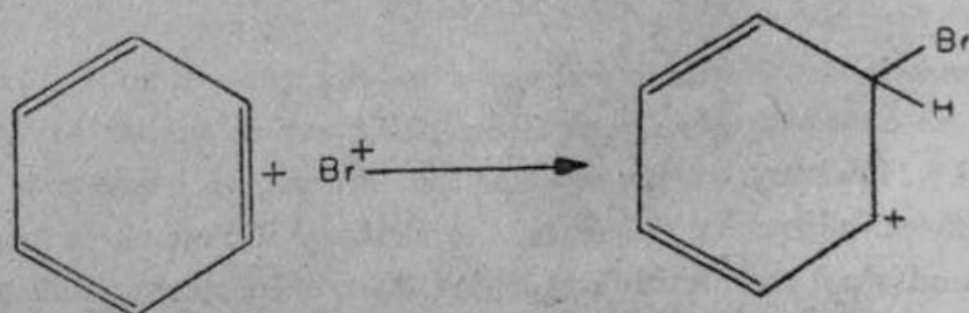
Let us consider the structure of a molecule of FeBr_3



The structure gives bromine the complete octet, but leaves Fe with only six electrons in the valence shell. In other words the valence shell of Fe is incomplete and hence would take up an electron pair to complete the octet. Now let us suppose a bromine molecule is at hand, the two could then "react" as follows :

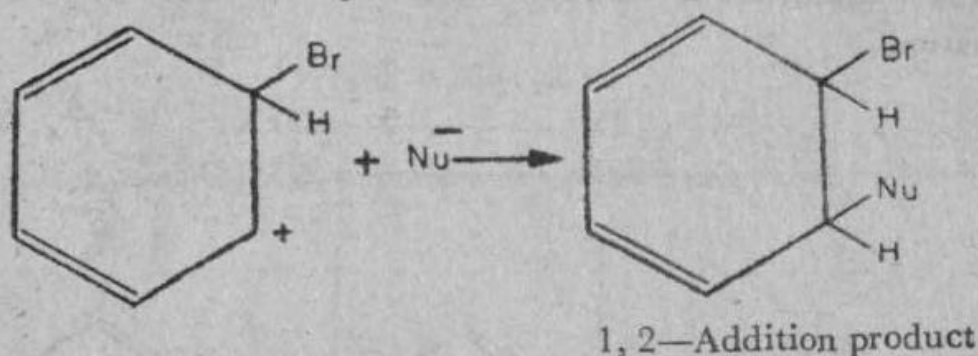


Formation of FeBr_4^- completes the octet of Fe, but in its wake produces a positively charged "bromonium ion". Obviously then, this, positively charged species is much more energetic than the one employed in an electrophilic attack on the π -electrons of alkenes. Hence it would attack the relatively stabilized π -electron system of benzene. The pattern of attack would be as follows (Fig. 18.12) :

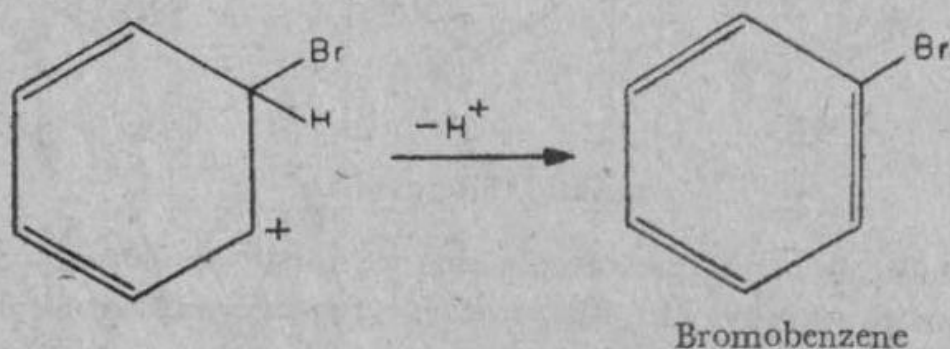


The positively charged benzene specie (let us call it "Benzenonium ion") has completely lost the extensive π -electron shield, and this loss would mean a corresponding loss in resonance stability and hence this specie would be energetically less stable and would react with either a nucleophile or eliminate a proton (*i.e.*, one positively charged hydrogen atom).

The attack of a nucleophile would give a 1,2—addition product,

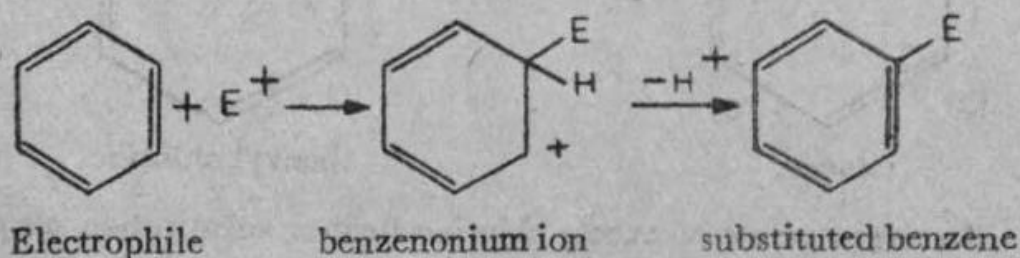


whereas elimination of a proton gives rise to substitution product.



The 1, 2—addition product is a simple alkene, whereas the substitution product *retains* the typical benzene structure. Hence the substituted benzene would retain the stability (due to resonance) whereas the 1, 2—addition product would obviously lack this stability. Therefore, “benzenonium ion” once formed would break up by loss of a proton reforming the parent benzene nucleus rather than undergo 1, 2—addition.

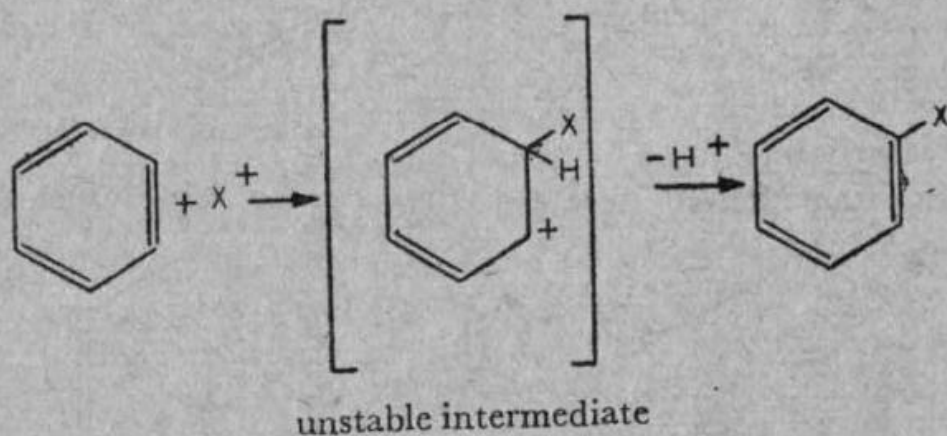
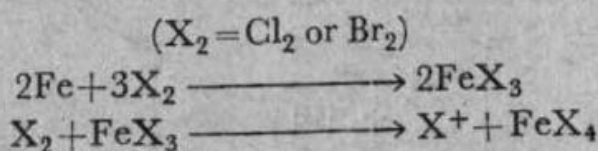
In short, the typical reactions of benzene are *electrophilic substitution* reactions brought about by *powerful* electrophiles. The general pattern of such reactions is depicted in the following equation :



The more important electrophilic substitution reactions of benzene are (a) halogenation, (b) nitration, (c) sulphonation, and (d) Friedel and Craft's reactions.

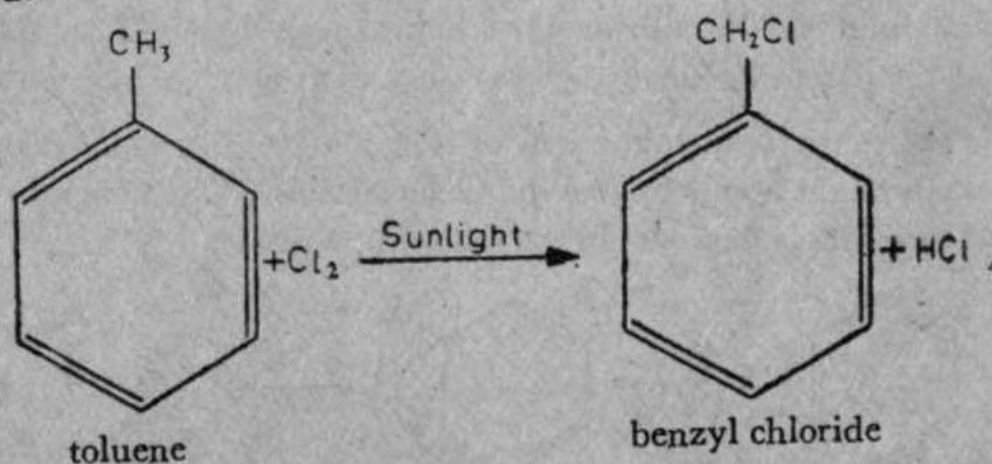
(a) **Halogenation** : Benzene is mixed with a halogen alongwith the corresponding ferric halide (as the catalyst). (The ferric halide may be produced by reaction of metallic iron with the halogen used

as the reagent). The reaction sequence is shown by the following equations :

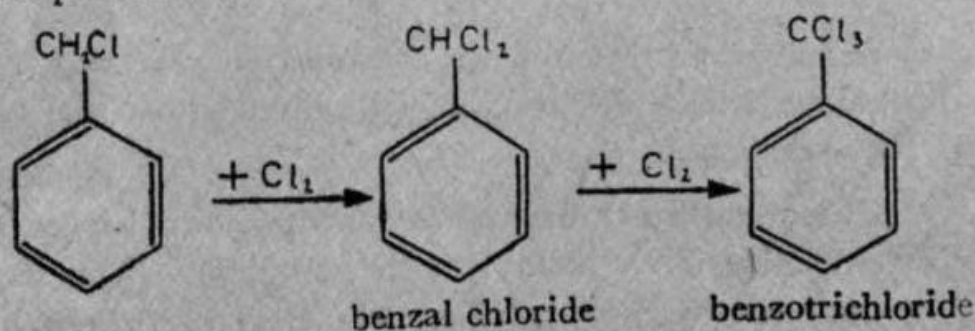


Only chlorination and bromination are usually employed. Iodination does not give good yield. Fluorination is too vigorous to control.

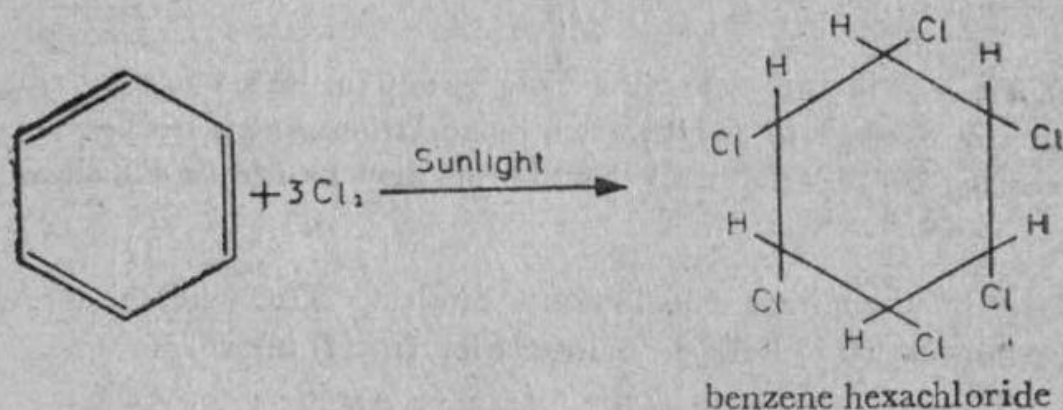
Chlorination or bromination must be carried out in the *absence* of sunlight. In the presence of sunlight, alkyl benzenes will rapidly react with Cl_2 or Br_2 by a photo-chemical process to substitute hydrogen of the alkyl group rather than the benzene ring. Thus toluene reacts as under :



In the presence of excess chlorine further substitution may occur.

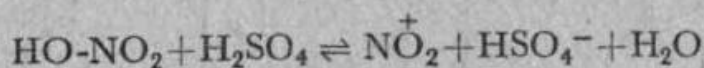


Benzene, under similar conditions, gives benzene hexachloride.



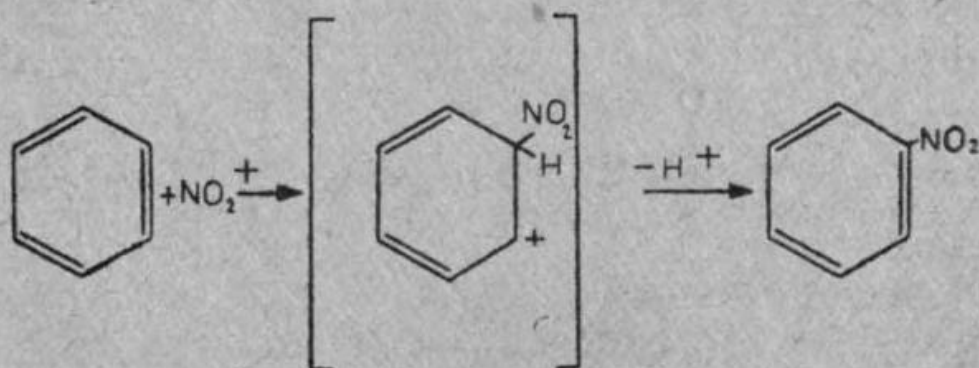
Nine isomers of hexachloride are possible, one of these is known as "gammexane" which is employed as an insecticide.

(b) **Nitration** : Nitration of benzene is done by warming benzene at 50°C with a 1 : 1 mixture of concentrated HNO_3 and H_2SO_4 . Nitric acid serves as source of the electrophilic nitronium ions (NO_2^+).



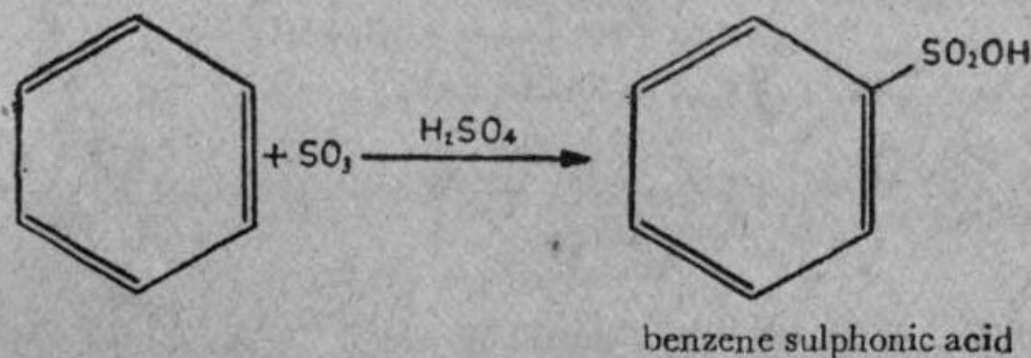
It is seen that H_2SO_4 aids in the formation of the nitronium ion.

The formation of nitrobenzene ($\text{C}_6\text{H}_5\text{NO}_2$) is indicated by the following equation :



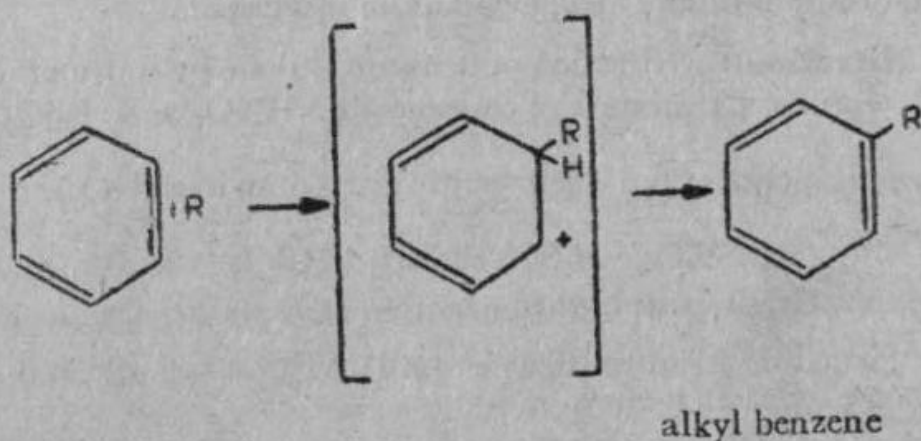
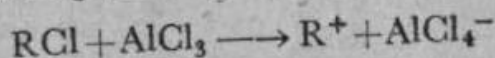
(c) **Sulphonation** : Substitution with a sulphonic acid group ($-\text{SO}_3\text{H}$) is carried out by mixing benzene with fuming H_2SO_4 (H_2SO_4 containing dissolved SO_3) or by warming with concentrated H_2SO_4 .

Probably the sulphonating agent is SO_3

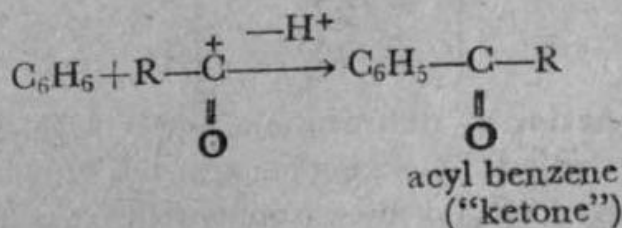
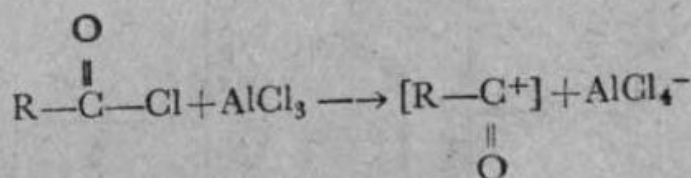


(d) **Friedel and Crafts Reactions :** The introduction of an

alkyl ($R-$) or an acyl ($R-\overset{\overset{O}{\parallel}}{C}-$) group in the benzene ring is commonly referred to as alkylation or acylation and is best performed by treating benzene with alkyl halide or acyl halide ($R-\overset{\overset{O}{\parallel}}{C}-Cl$) in the presence of aluminium chloride as a catalyst. The function of $AlCl_3$ is the same as that of $FeBr_3$ in halogenation (see (a) above).



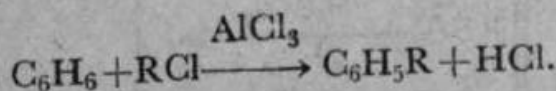
Similarly



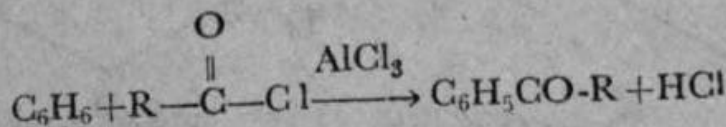
Aluminium chloride is regenerated :



The net reaction may then be represented as :

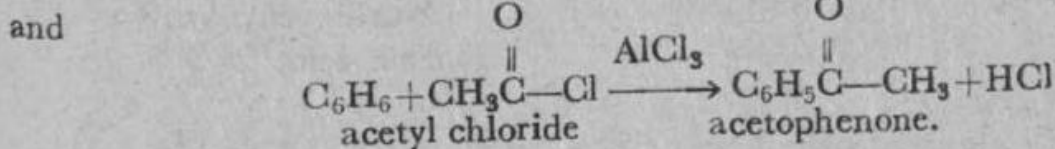
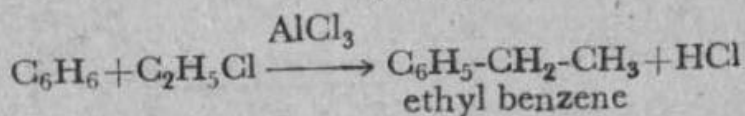
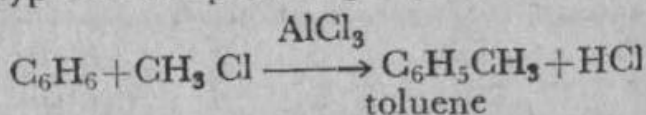


and



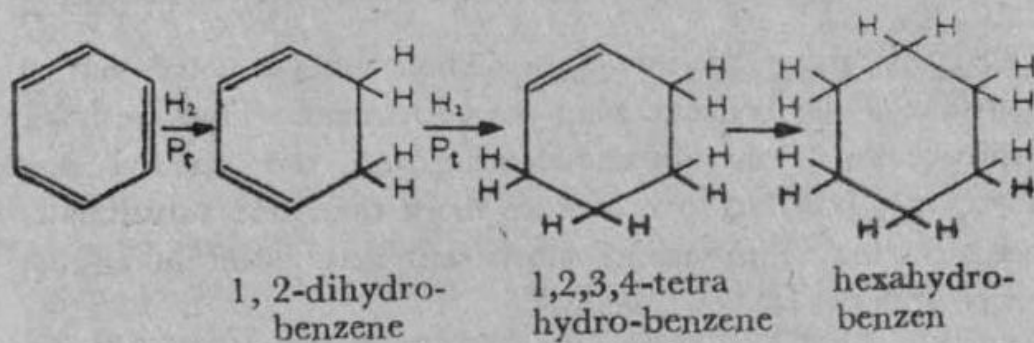
The reaction is performed at ordinary temperature and in the presence of inert solvents, like carbon disulphide (CS_2). Anhydrous aluminium chloride is usually employed.

Some typical examples are given below :



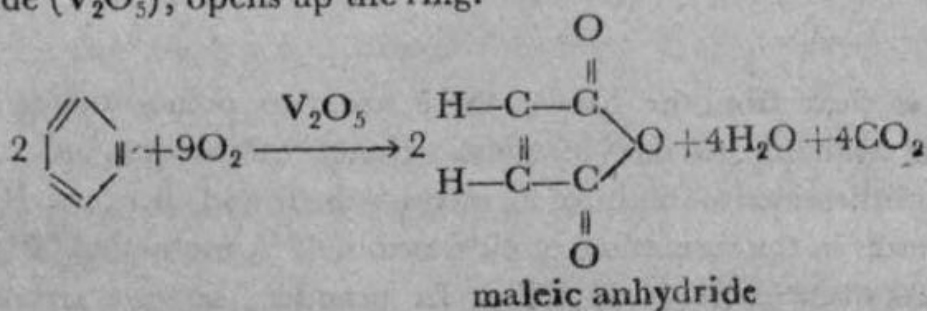
(b) REACTIONS IN WHICH THE BENZENE RING IS NOT RETAINED

(i) **Reduction :** Benzene will add 3 molecules of H_2 when the reaction is carried out at elevated temperature and in the presence of platinum in acidic solvents such as acetic acid.

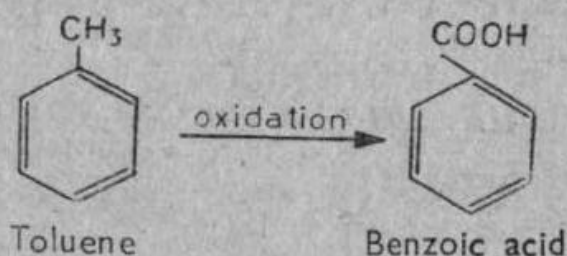


1, 2—Dihydro and 1, 2, 3, 4—tetrahydro benzenes are not prepared by this method, because once 1, 2—dihydro benzene is formed, the molecule assumes a simple olefinic structure and as such further addition of hydrogen becomes rapid.

(ii) **Oxidation :** Benzene is not oxidized by permanganate or potassium dichromate at room temperature. However, heating with air at high temperature, in the presence of a catalyst, vanadium pentoxide (V_2O_5), opens up the ring.



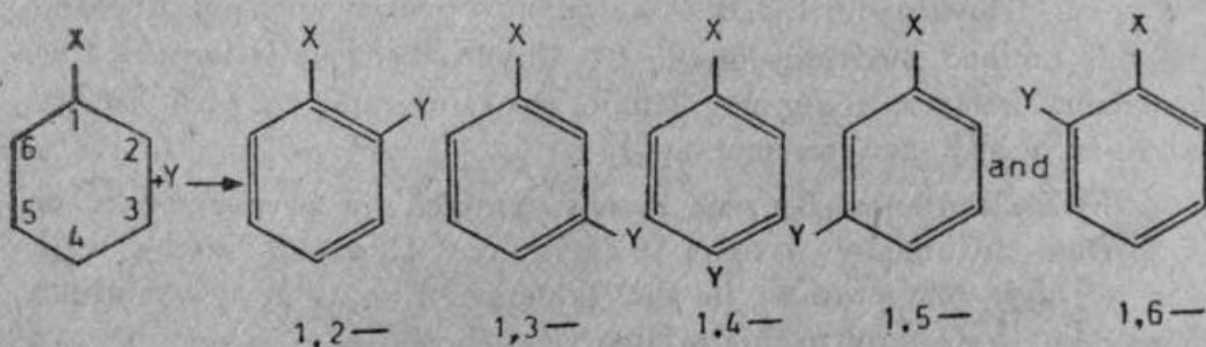
Alkyl substituted benzenes, on the other hand, are readily oxidized by aqueous potassium permanganate or acidified potassium dichromate solution, *e.g.*, toluene gives benzoic acid on treatment with aqueous KMnO_4 .



It has been observed that *one* alkyl group, whatever its length, is oxidized to *one* carboxylic ($-\text{COOH}$) group, in such reactions (Formation of acids serves as a test for alkyl benzenes as the colour of KMnO_4 is discharged in the process.)

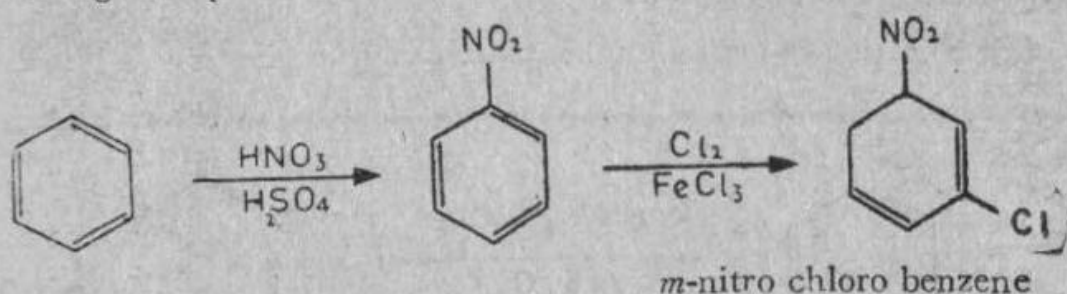
ORIENTATION IN SUBSTITUTION REACTIONS

While discussing the structure of benzene we noted that all the six positions of the benzene ring are equivalent. Thus we have only one nitrobenzene, one bromobenzene and one methyl benzene. However, it is possible to introduce more than one substituents into the benzene ring. The second substituent may enter in any of five vacant positions as is shown below :

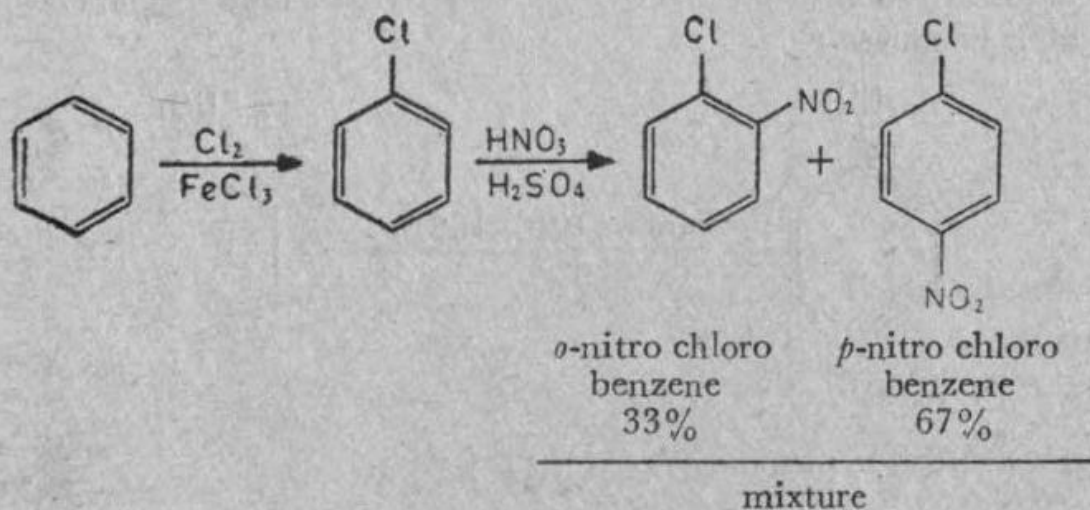


As is clear from the above there are two ortho- and two meta-positions available to one of para. Hence calculating on a chance basis, substitution of Y into a mono substituted benzene ($\text{C}_6\text{H}_5\text{X}$) would result in the formation of 40% ortho, 40% meta- and 20% para-disubstituted benzene ($\text{C}_6\text{H}_4\text{XY}$). In practice, however, results are

obtained which do not agree with the above chance substitution ratio. Following examples are illustrative.



m-Nitro chlorobenzene is the main product.



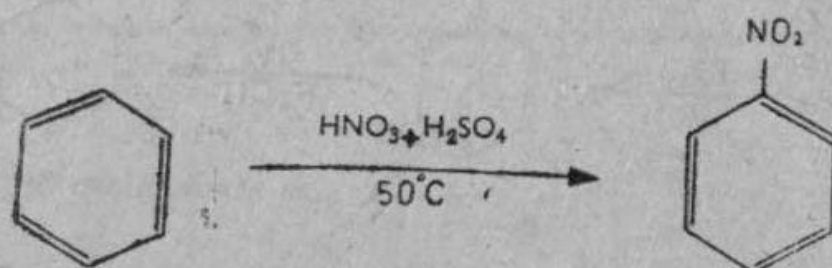
We observe that nitration followed by chlorination yields mainly the meta-isomer, but the reverse process gives rise to a mixture of ortho- and para-isomers. We might then conclude that the group X which is already present in the benzene ring determines the position which, will be taken by the entering group Y. Thus $-\text{NO}_2$ group directs the $-\text{Cl}$ group to meta-position, whereas the $-\text{Cl}$ group directs the $-\text{NO}_2$ group to ortho and para-positions.

Other substituent groups have a directive influence on the entering of the second substituent similar to that of either the directive influence of $-\text{NO}_2$ group or the $-\text{Cl}$ group. It has been observed that presence of $-\text{NO}_2$ or a $-\text{SO}_2-\text{OH}$ group in the benzene ring directs the entering group to meta-position, where as presence of a halogen or an alkyl group directs the entering group to an ortho- and para-position.

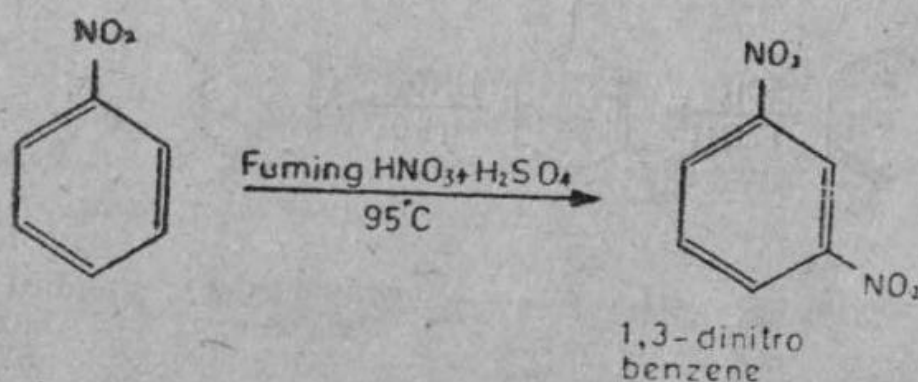
The presence of a substituent greatly effects the reactivity of the benzene ring towards further attack by other electrophilic reagents. It has been observed that a meta-directing group, if present, greatly reduces the reactivity of the ring, where as, an ortho- or para-directing

group greatly enhances the reactivity of the ring. The following examples are illustrative of this phenomenon :

(a) Nitration of benzene takes place at 50°C .

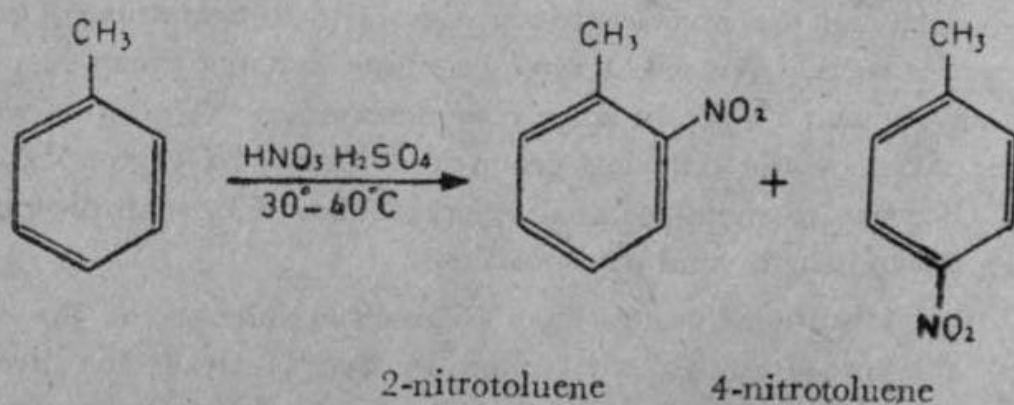


For dinitration to be effective *fuming* HNO_3 at higher temperature has to be employed :

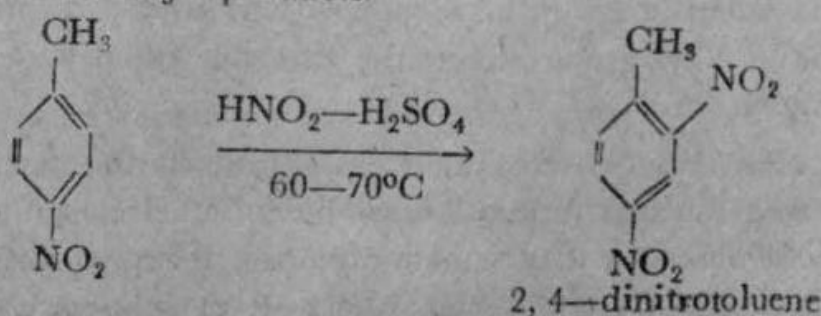


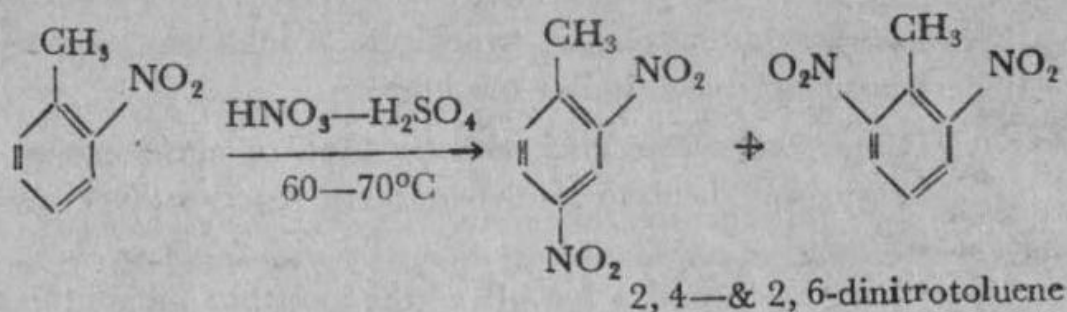
it is difficult to introduce the third $-\text{NO}_2$ group.

On the other hand nitration of toluene takes place with HNO_3 and H_2SO_4 mixture at $30-40^{\circ}\text{C}$:

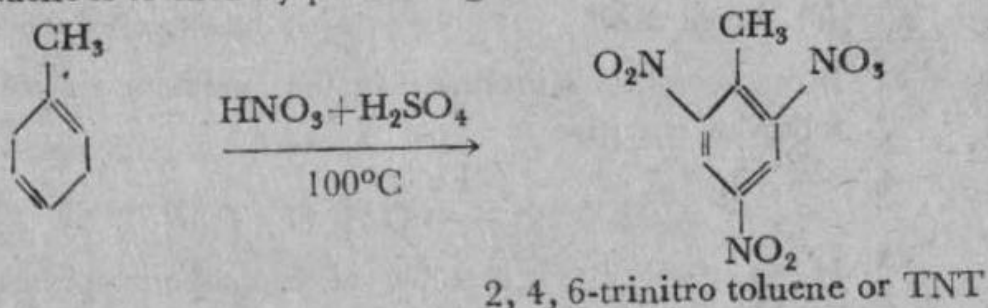


if the temperature is raised to $60-70^{\circ}\text{C}$ dinitro—rather than mononitro—toluenes are the major products.





So strong is the activating influence of the methyl group that 2, 4, 6-trinitro toluene is formed by performing the reaction at 100°C :

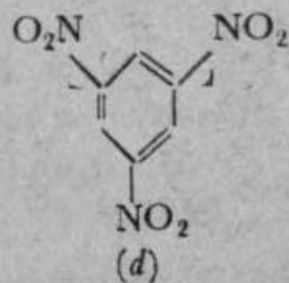
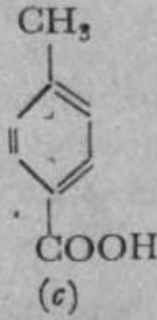
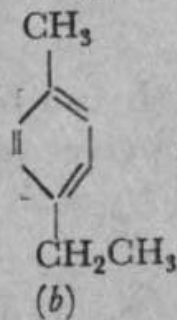
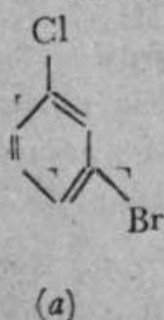


TNT is a very powerful explosive.

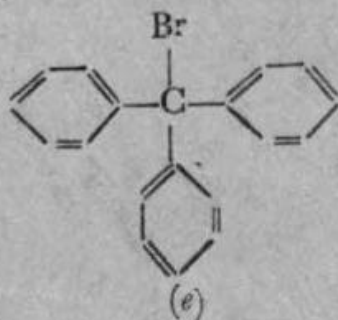
Therefore, it is worthwhile to remember that an ortho or a para-directing group, if present, activates the benzene ring and makes an electrophilic attack much easier than when a meta-directing group is present on the ring.

Questions

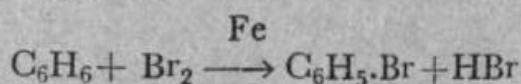
- Write structural formulas for the following compounds :
 - nitrobenzene,
 - benzene sulphonic acid,
 - acetophenone, and
 - p*-bromobenzoic acid.
- Name the following compounds :



and

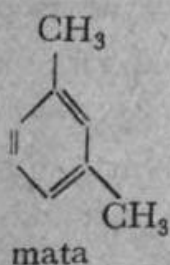
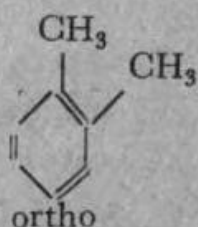


3. Benzene has a planar structure. Would you expect cyclohexane to have a similar structure?
4. Compare the reactions with bromine of cyclohexane, cyclohexene and benzene with regard to reaction type and conditions.
5. Write the formulas for all or the possible monobromo derivatives of each of the following compounds :
 - (a) ethyl benzene,
 - (b) *o*-dichlorobenzene,
 - (c) toluene and
 - (d) benzene sulphonic acid.
6. Bromo-benzene is prepared in the laboratory according to the following equation :

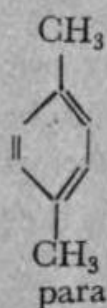


If 40 g of Br_2 give 30g of bromobenzene, calculate the % percentage yield. (Ans. 75%)

7. A benzenoid liquid (A) of molecular formula C_8H_{10} is oxidized to a dicarboxylic acid. Nitration of A gives only one mono-nitro derivative. What is the structural formula of A?
8. The three isomeric *o*—, *m* and *p*—xylenes possess the following formulae :

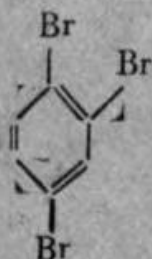
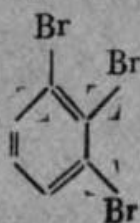


and

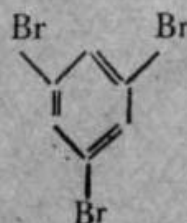


o-xylene on mono-nitration gives two isomeric nitroxylenes, *m*-xylene gives three and *p*-xylene gives only one nitroxylene. Write down the structural formulas of all the isomeric nitroxylenes.

9. Three isomeric tribromobenzenes having the following formulae are known :



and



When each is nitrated so as to introduce only one nitro group, they give, respectively two, three and one mono nitro tribromo-benzenes. Assign structures to these compounds.

10. Would ethyl benzene be the only organic product from the reaction : bromobenzene + ethyl bromide + sodium? Explain with equations.
 11. Describe a chemical test that can be used to distinguish between :
 - (a) benzene and cyclohexene,
 - (b) phenyl ethene and phenyl ethane,
 - (c) benzene and toluene,
 - (d) toluene and *o*-xylene,
 - (e) benzyl chloride and *p*-chlorotoluene.
 12. Write a probable mechanism by which iron wire acts as a catalyst for the halogenation of benzene.
 13. Indicate the main substitution products in each of the following reactions :
 - (a) toluene + chlorine (Fe catalyst),
 - (b) ethyl benzene + potassium permanganate (heat),
 - (c) toluene + acetyl chloride (AlCl_3 catalyst),
 - (d) nitrobenzene + conc. H_2SO_4 (heat),
 - (e) iodobenzene + bromine (Fe catalyst),
 - (f) Toluene + CH_3I (AlCl_3 catalyst),
 - (g) Toluene + Br_2 (catalysed by sunlight).
-

CHAPTER 19

NATURAL PRODUCTS

In Chapter 11, it was mentioned that the name "organic chemistry" implied chemistry of compounds derived from living sources, *i.e.*, plants and animals. Diverse and extensive, as plant and animal kingdoms are, so is the chemistry of compounds derived from these sources. With the space at our disposal it is possible to give only a very brief description of the more important and abundant organic substances that are derived mostly from plant sources. However, it might be emphasized that the following description does not cover all the important types. This discussion will serve as an introduction to especially those natural products that have bio-chemical importance.

Natural products, then, may be divided into the following groups :

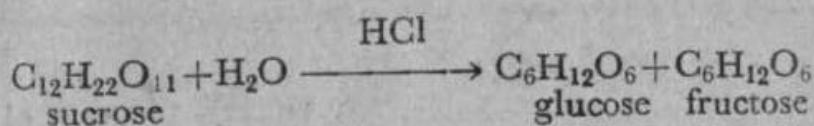
- (a) Carbohydrates.
- (b) Proteins and amino acids.
- (c) Terpenes.
- (d) Alkaloids.
- (e) Steroids.
- (f) Vitamins.
- (g) Fats and Oils.

(a) **Carbohydrates :** They are compounds of carbon, hydrogen and oxygen, and include sugars, starches, cellulose and related substances. They are found, as we all know, in the roots, the stems and the leaves of plants. Carbohydrates, besides forming an important constituent of our diet, find extensive application in paper, textile and allied industries.

Carbohydrates have the general formula $C_m(H_2O)_n$ where m and n are small numbers. They are essentially poly-hydroxy aldehydes or polyhydroxy ketones or yield such compounds upon hydrolysis with a mineral acid. Carbohydrates are broadly divided into three groups :

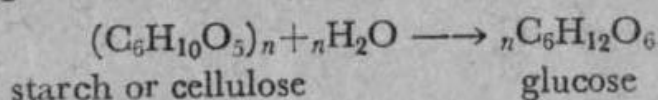
(i) **Mono-Saccharides :** These are the simplest carbohydrates and are further sub-divided into *aldoses* and *ketoses* depending upon whether the main functional group is *aldehydic* or *ketonic* respectively. Glucose and fructose (both have the formula $C_6H_{12}O_6$) are important members of this group. The former is an aldose and the latter a ketose

(ii) **Disaccharides** : These are made of two monosaccharide units and on hydrolysis give the constituent monosaccharides. Sucrose ($C_{12}H_{22}O_{11}$), commonly known as cane sugar, is a typical disaccharide and gives glucose and fructose on hydrolysis with hydrochloric acid.



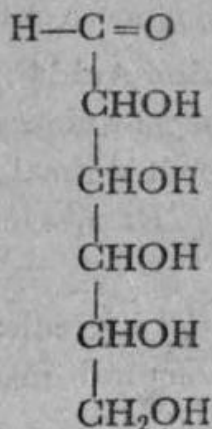
Sucrose, then, is an "anhydride" of glucose and fructose.

(iii) **Polysaccharides** : They contain many monosaccharide units. Typical examples are starch ($(C_6H_{10}O_5)_n$) obtained mainly from potatoes, and *cellulose*, $(C_6H_{10}O_5)_n$ obtained largely from cotton and wood pulp. The molecular size of these compounds becomes obvious from the fact that the value of n for starch is more than 500, while for cellulose it is between 1000—3000. Both starch and cellulose are built up of glucose units and yield the same upon hydrolysis :—



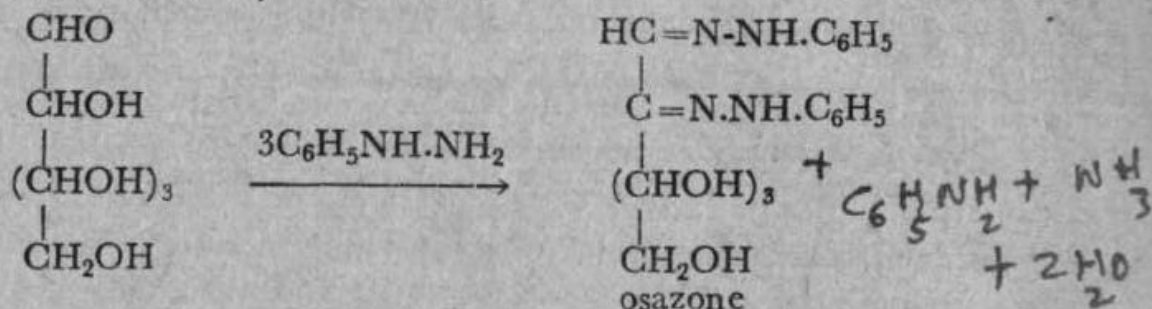
Glucose : Glucose, which occurs in grape sugar, is a white crystalline solid, and is soluble in water. Glucose is obtained, on a commercial scale, by the hydrolysis of starch with hydrochloric acid.

Chemical character of glucose is borne out by the fact that it reduces Fehling solution and gives a silver mirror with Tollen's reagent. These properties indicate the presence of an aldehydic group in the molecule. Glucose is acetylated with acetic anhydride forming a pentacetate, thus showing the presence of five hydroxy groups in the molecule. All these and other properties indicate that glucose has the following structure :

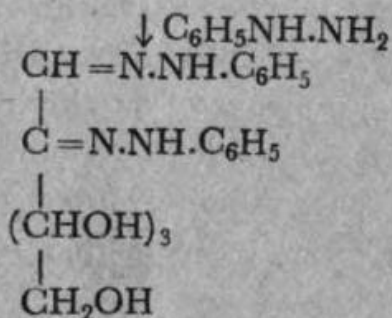
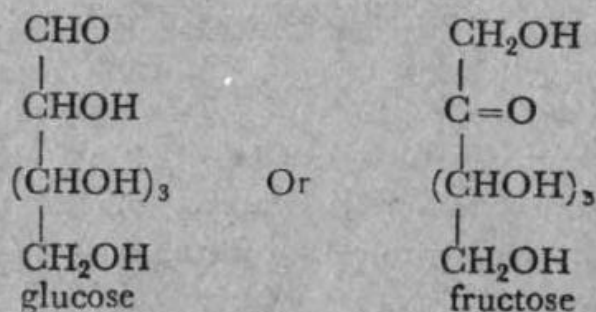


An important reaction of mono-saccharides is the one with phenyl hydrazine, $C_6H_5NH.NH_2$:

Glucose forms a yellow "osazone" :—



Fructose, which is found in honey, has the same formula as glucose, but its chemical reactions indicate the presence of a ketonic group, and also the five hydroxy groups in the molecule. However on treatment with phenyl hydrazine, an "osazone" identical to the one formed by glucose is obtained. This property clearly indicates that glucose and fructose have the same structure at carbon atoms other than the first two carbons. This is borne out by the following structures :



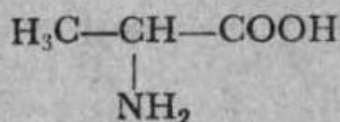
Osazone obtained from glucose or fructose.

(b) **Proteins and Amino Acids** : Proteins are the most complex naturally occurring organic substances. They are of primary importance to the structure of both animal and plant tissue. Proteins are widely distributed in nature. Hair, skin, horns, hoofs, etc., are essentially all proteins.

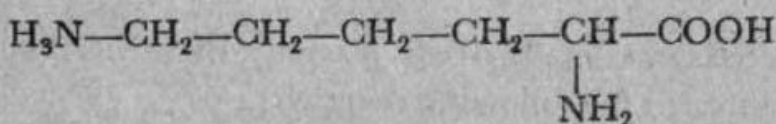
Proteins are an essential ingredient of our diet. In fact it is said that proteins serve as structural material for animals, just as the polysaccharides do for plants.

Proteins are polymeric substances and on treatment with hydrochloric acid are hydrolysed to a mixture of α -amino acids. Thirty different amino acids have, been identified. These amino acids may be divided into three groups :—

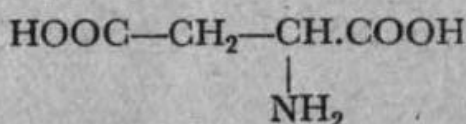
(i) **Neutral Amino Acids :** They contain one amino group and one carboxylic group, *e.g.*, *alanine*,



(ii) **Basic Amino Acids :** They contain *two* amino groups and one carboxylic group, *e.g.*, *lysine*

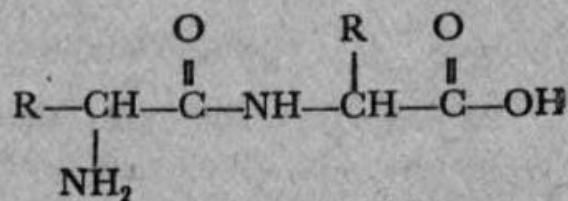
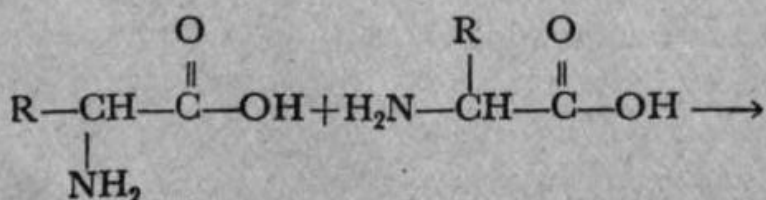


(iii) **Acidic Amino Acids :** They contain one amino and two carboxylic groups, *e.g.*, *aspartic acid*,



Some amino acids have been found to be essential to life in the animal body. They cannot be synthesized in the body and hence must be present in the diet. Absence of any of these amino acids leads to some form of malnutrition.

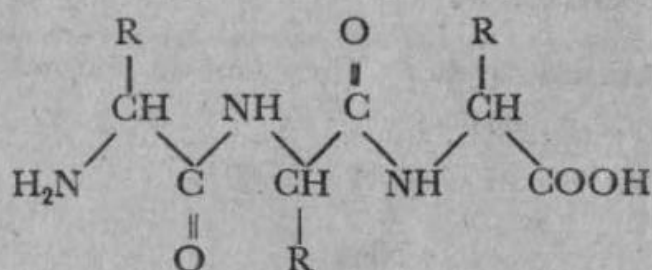
The fact that amino acids are obtained on hydrolysis of proteins suggests that proteins are built up of amino acid units. This prompted the German chemist, Emil Fischer, to put forth the *Peptide, theory* of the structure of proteins. This theory assumes that amino acids are present in proteins as long chains joined together by *amide linkages*, formed between amino group of one amino acid and the carboxylic group of another. Such linkages are referred to as *peptide bonds*: *Linkage*.



peptide bond

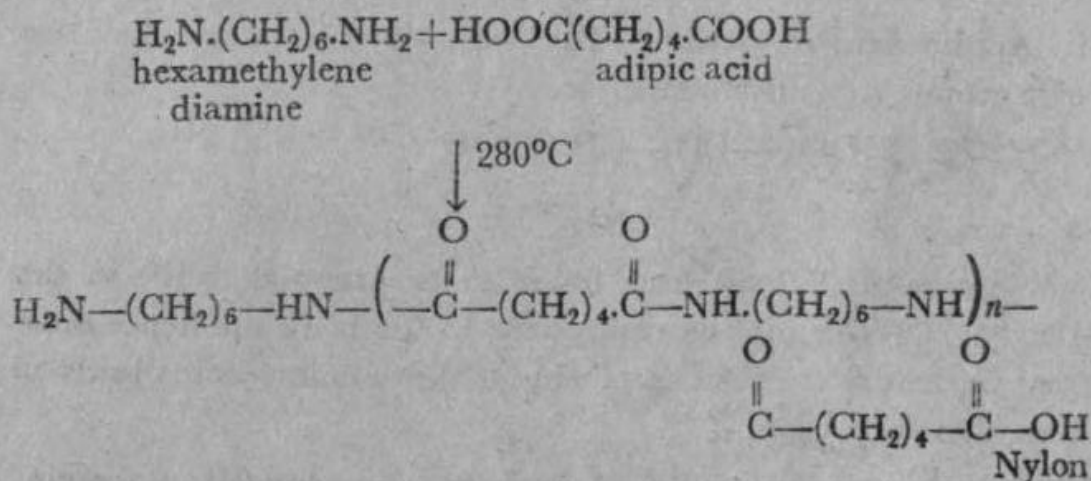
There is considerable evidence in support of the peptide structure of proteins.

Proteins are hence represented by the partial structure



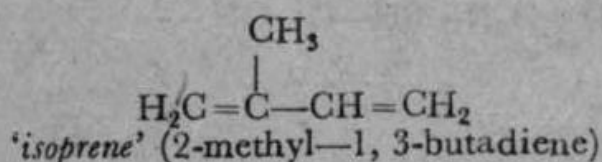
So that a free amino group and free carboxylic group occupy the two ends of the chain. (R stands for any amino acid).

Nylon which is man-made silk (a protein), likewise is a polypeptide. It is obtained through the following reactions :



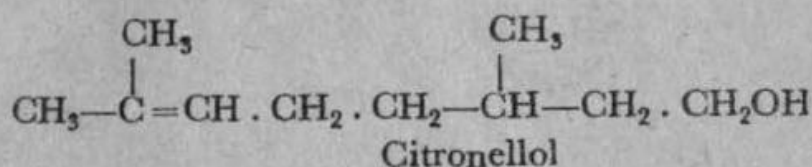
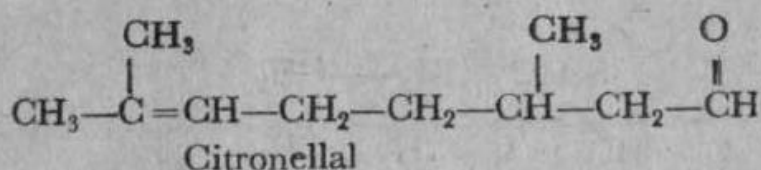
(c) **Terpenes** : Most plant materials give volatile, fragrant substances on steam distillation. Such substances are termed *essential oils* and are used as flavours, perfumes and medicinals. Many of these substances belong to yet another class of organic compounds called *terpenes*.

Terpenes are unsaturated hydrocarbons with the molecular formula $C_{10}H_{16}$. They possess a typical structure which is built up of "isoprene" units :

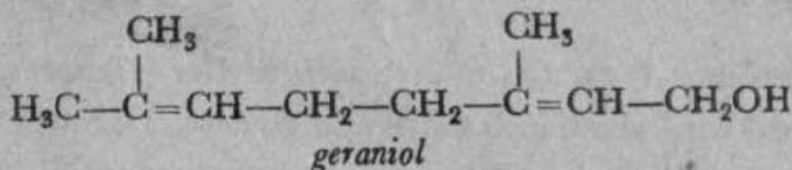


Terpenes may be open chain or cyclic compounds containing two isoprene units or they may contain three isoprene units (*sesquiterpenes*). *Diterpenes* contain four isoprene units and so on.

Citronellal which occurs in lemon oil and *citronellol* which occurs in rose oil have the following structures :

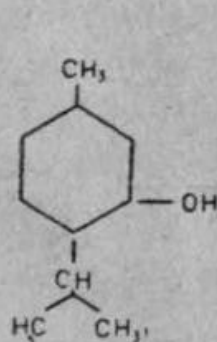


Rose oil, extracted from petals, contains 20—40% citronellol and 40—60% of another terpene, *geraniol* :

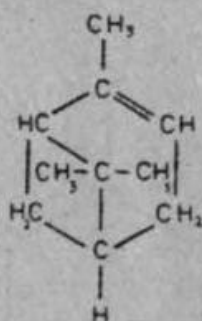


Structural similarity of the three is obvious.

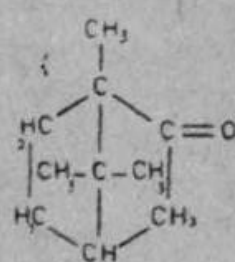
Peppermint oil consists chiefly of *menthol*, whereas the chief constituent of turpentine oil is *pinine*. Similarly *camphor* is obtained from camphor tree.



Menthol



Pinine

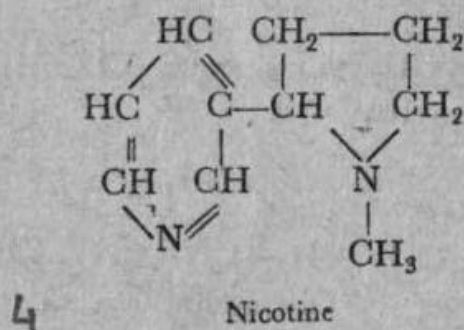


Camphor

(d) **Alkaloids** : They are nitrogen containing basic substances, usually obtained from plants and possess marked physiological action. Alkaloids are usually extracted from plants by digesting the plant material with dilute mineral acids. The alkaloids are obtained as water soluble salts.

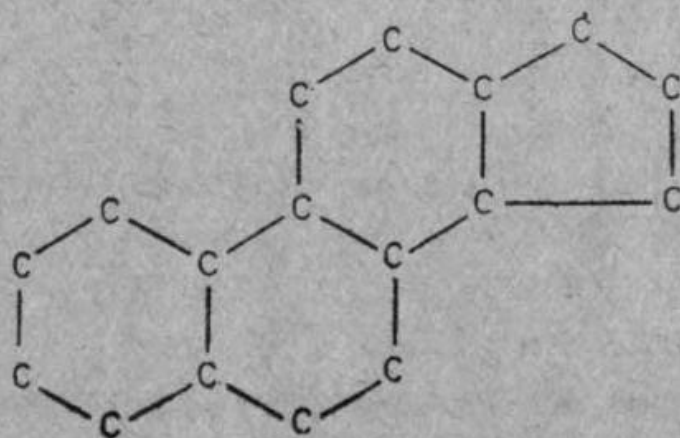
Most of the alkaloids are solids and have complex structures. They have a very bitter taste and are highly poisonous.

Nicotine, one of the simplest alkaloids, is present in tobacco leaves (4—6% by weight of dry leaves). It has the following structure :



Quinine ($C_{20}H_{24}N_2O_2$) is obtained from the bark of cinchona tree and is largely used for the treatment of malaria.

(e) **Steroids.** Fats, as we have seen earlier (Chapters 15 and 17) are hydrolysed with alkali into soaps and glycerol. However, a portion of these fats remains unchanged on treatment with alkali. This portion consists of substances which are alcoholic in nature and are called *sterols*. A common feature of their chemical structure is a system of four fused carbon rings; three with six members and the fourth with five. These seventeen carbons, are then, linked in the following framework :

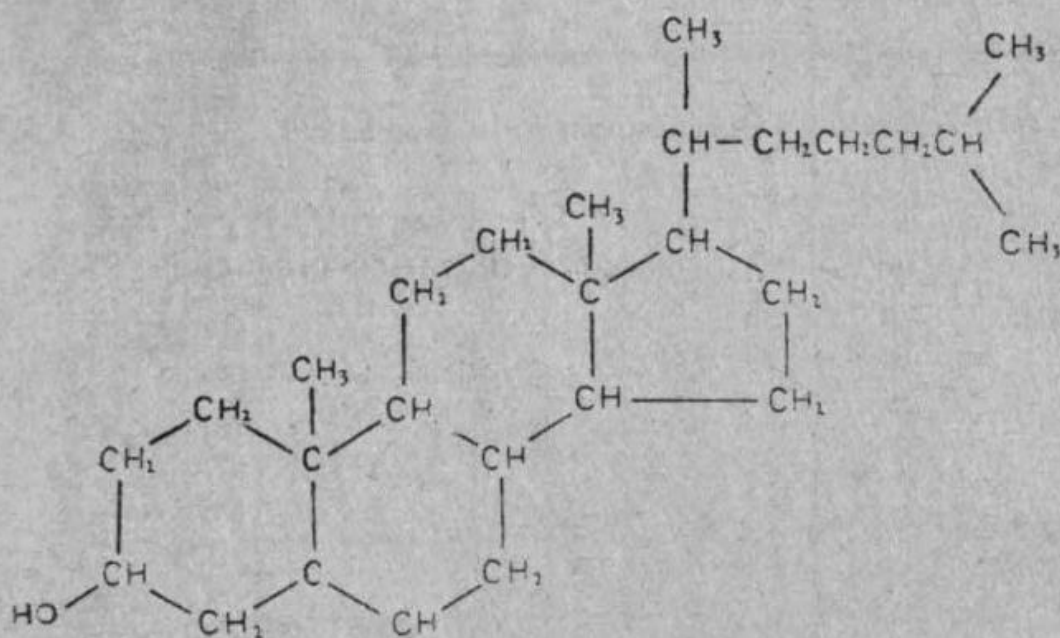


Sterol framework

The rings are usually not aromatic in character.

The carbon skeleton of sterols, shown above, is present in a large number of biologically important materials. The more important are the *bile acids*, *sex hormones* and *vitamin D*. These compounds are commonly called *steroids* and perform important functions in the animal body.

Cholesterol is the most common sterol and occurs in larger amounts in brain and spinal cord. It is the chief constituent of gall stones.



Cholesterol

(f) **Vitamins** : The necessity of proteins, carbohydrates, fats and minerals in our diet has been recognised from early times. However, in early twentieth century it was shown that if highly purified forms of the above diet were fed to animals, their normal growth was greatly hampered. Soon it was realised that additional substances were required to sustain body growth. Such accessory dietary factors are called *vitamins* and derive their name from first vitamin *Thiamine*, which incidentally happens to be an amine.

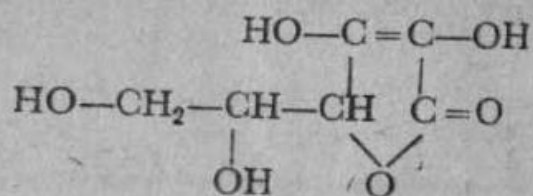
It should be understood that vitamins do not constitute food in themselves, they probably act as catalysts or promoters in the metabolic process, and hence are used in small amounts only.

Vitamins have complex structures and are usually named as vitamin A, B₁, B₂, C, D and so on.

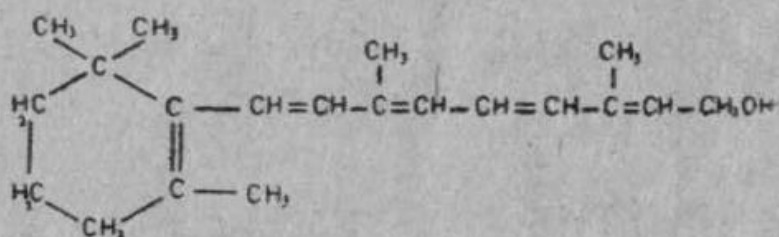
Vitamins are of two types : (i) *Water soluble vitamins*. Examples are vitamin B₁ (thiamine) and vitamin C (ascorbic acid).

(ii) **Oil Soluble Vitamins** : Examples are vitamin A (a terpene derivative) and vitamin D (a steroid).

Vitamin C has the following structure



Vitamin A has four isoprene units in its molecule :



Vitamin A

END

THE PERIODIC TABLE OF THE ELEMENTS

(WITH ATOMIC NUMBERS)

GROUP	I ^A	II ^A	III ^A	IV ^A	V ^A	VI ^A	VII ^A	VIII	I ^B	II ^B	III ^B	IV ^B	V ^B	VI ^B	VII ^B	0		
1	H ₁														(H) ₁	He ₂		
2	Li ₃	Be ₄														Ne ₁₀		
3	Na ₁₁	Mg ₁₂														Ar ₁₈		
4	K ₁₉	Ca ₂₀	Sc ₂₁	Ti ₂₂	V ₂₃	Cr ₂₄	Mn ₂₅	Fe ₂₆	Co ₂₇	Ni ₂₈	Cu ₂₉	Zn ₃₀	Ga ₃₁	Ge ₃₂	As ₃₃	Se ₃₄	Br ₃₅	Kr ₃₆
5	Rb ₃₇	Sr ₃₈	Y ₃₉	Zr ₄₀	Nb ₄₁	Mo ₄₂	Tc ₄₃	Ru ₄₄	Rh ₄₅	Pd ₄₆	Ag ₄₇	Cd ₄₈	In ₄₉	Sn ₅₀	Sb ₅₁	Te ₅₂	I ₅₃	Xe ₅₄
6	Cs ₅₅	Ba ₅₆	La ₅₇	Hf ₇₂	Ta ₇₃	W ₇₄	Re ₇₅	Os ₇₆	Ir ₇₇	Pt ₇₈	Au ₇₉	Hg ₈₀	Tl ₈₁	Pb ₈₂	Bi ₈₃	Po ₈₄	At ₈₅	Rn ₈₆
7	Fr ₈₇	Ra ₈₈	Ac ₈₉															

LANTHANIDES	Ce ₅₈	Pr ₅₉	Nd ₆₀	Pm ₆₁	Sm ₆₂	Eu ₆₃	Gd ₆₄	Tb ₆₅	Dy ₆₆	Ho ₆₇	Er ₆₈	Tm ₆₉	Yb ₇₀	Lu ₇₁
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ACTINIDES	Th ₉₀	Pa ₉₁	U ₉₂	Np ₉₃	Pu ₉₄	Am ₉₅	Cm ₉₆	Bk ₉₇	Cf ₉₈	Es ₉₉	Fm ₁₀₀	Md ₁₀₁	No ₁₀₂	Lw ₁₀₃
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